UNIVERSITÉ DE MONTRÉAL

DIFFUSION DE LA MATIÈRE DANS LES POLYMÈRES

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RÉSUMÉ

Lors de l'étude des mélanges solvants-polymère soumis ou non à un écoulement externe, les observations expérimentales convergent, à quelques exceptions, vers l'importance du couplage qui survient entre la diffusion, l'écoulement et la déformation de la microstructure du polymère et qui influe sur leurs comportements respectifs. La séparation de phase, la formation de nouvelles morphologies, la migration à travers les lignes de courant, etc. sont les quelques comportements induits par écoulement et qui sont observés dans les solutions semi-diluées de polymères dans lesquelles ce couplage se manifeste explicitement. L'effet de ce dernier n'est toutefois pas limité qu'aux systèmes en écoulement imposé, mais il a été observé, à maintes reprises, durant les processus de transfert de masse dans les systèmes en équilibre mécanique. En effet, les mesures obtenues à partir des expériences classiques de la diffusion (sorption, désorption, perméation, pervaporation etc.) d'un ou de plusieurs solvants dans un polymère restent généralement indescriptibles par les lois linéaires et simples de Fick. L'une des causes principales de ces comportements réside dans le caractère non-linéaire et individuel de la microstructure qui détermine les propriétés les plus essentielles des polymères.

Dans le travail de cette thèse, nous nous sommes proposés de contribuer à la compréhension des phénomènes mentionnés ci dessus et d'élucider l'influence du couplage précité sur leurs comportements. Dans cette perspective, nous avons développé, à l'aide du formalisme GENERIC (General Equation for Non-Equilibrium Reversible and Irreversible Coupling), de nouvelles formulations mathématiques capables de décrire les observations expérimentales restées encore réfractaires aux théories existantes. Les systèmes auxquels nous nous sommes intéressés sont les mélanges miscibles de type : i) binaires constitués d'un fluide simple (solvant) et d'un fluide complexe (polymère) et ii) ternaires composés de deux fluides simples (solvants) et d'un fluide complexe (polymère). Les équations GENERIC gouvernant l'évolution temporelle de ces systèmes

sont paramétrées par l'énergie libre et par les temps de relaxation qui expriment le caractère d'individualité du mélange considéré.

Durant la dernière décennie, il s'est avéré que pour décrire correctement le comportement dynamique d'un mélange binaire, il est préférable de le considérer comme formé de deux fluides, dont chacun est caractérisé par ses propres variables d'état, qui sont, dans le cadre de l'hydrodynamique classique, sa densité de masse ρ_i, et son vecteur densité de la quantité de mouvement $\mathbf{u}_i$ (l'indice i désigne le fluide i=1,2). La contribution de la structure interne du polymère est souvent décrite soit par la fonction de distribution de l'espace de configuration ψ ou par le tenseur de conformation du second ordre $\mathbf{m}$. Les variables d'état correspondant au mélange sont alors obtenues par le biais d'une transformation biunivoque adéquatement choisie. Dans le cas des mélanges binaires (articles 1, 2 et 3), les variables d'état se résument à la densité de la masse totale ρ, au vecteur densité de la quantité de mouvement globale $\mathbf{u}$, à la fraction massique c_1 et au vecteur densité de la quantité de mouvement relative $\mathbf{w}_1$ d'une composante, et au tenseur symétrique du second ordre $\mathbf{m}$ décrivant la microstructure. Pour les systèmes ternaires (étudiés dans les articles 4 et 5), nous avons introduit le concept du modèle à trois fluides qui étend l'idée du modèle à deux fluides utilisé pour les systèmes binaires. Dans ce cas-ci, les variables d'état incluent, en plus de celles choisies pour le mélange à deux composants, la fraction massique c_2 et le vecteur densité de la quantité de mouvement relative $\mathbf{w}_2$ du deuxième composant.

Les équations d'évolution des mélanges miscibles binaires (Article 1) et ternaires (Article 4) soumis à un écoulement externe, montrent explicitement que, la diffusion dépend anisotropiquement de l'écoulement et de la déformation de la structure interne. Réciproquement, la structure interne est influencée, d'une manière concomitante, par les deux types d'écoulement : externe et interne. Le dernier est produit, bien sûr, par la diffusion. Outre cette mutuelle dépendance, des contraintes élastiques sont créées au sein du mélange par les mouvements relatifs (flux de diffusion) et par conséquent modifient le comportement dynamique de l'écoulement. De plus, par la nature même des systèmes ternaires, de nouveaux couplages apparaissent entre les flux de masse des deux

composants dus aux effets d'entraînement. Dans le processus de la résolution asymptotique des équations d'évolution, nous avons calculé les coefficients de transport en fonction des temps de relaxation et en terme des coefficients de friction. Dans le régime non linéaire, ces coefficients dépendent explicitement du gradient de la vitesse d'écoulement $\kappa_{\alpha\beta} = \partial v_\beta / \partial r_\alpha$ rendant le processus de la diffusion fortement anisotrope même en l'absence des contraintes internes produites par la déformation de la structure interne.

En l'absence d'un écoulement externe, le couplage diffusion-déformation engendre dans les systèmes binaires et ternaires de nouveaux comportements communément appelés non-Fickiens ou viscoélastiques. Leur description requiert, dans le cadre des modèles développés pour les systèmes en écoulement, l'application des contraintes de l'équilibre mécanique et de l'incompressibilité totale. Par conséquent, la densité de la masse totale ρ (incompressibilité globale) et le vecteur densité de la quantité de mouvement global $\mathbf{u}$ (absence d'écoulement) deviennent des variables thermodynamiques dépendantes et doivent être exclues de l'ensemble des variables d'état.

La diffusion non-Fickienne d'un solvant dans un polymère en l'absence d'un écoulement externe (articles 2 et 3) est décrite par le modèle, appelé (c,w,m)-model, dans lequel l'inertie du flux de masse vient s'ajouter à celle de la conformation pour tenir compte de tous les effets inertiels. L'étude de certaines observations bien connues du processus de la diffusion nous a conduit à déduire de nouvelles formulations simplifiées qui sont obtenues par réduction de ce modèle. Parmi ces modèles réduits, le (c,w)-model, dans lequel l'influence de la microstructure est exprimée indirectement par le biais des relations constitutives, décrit, malgré sa simplicité, plusieurs comportements non-Fickiens et en particulier la diffusion Cas II, appelée aussi onde de choc d'Alfrey due à sa ressemblance avec la propagation d'ondes typiquement non linéaires. Pour expliquer ce comportement, nous avons introduit un nouveau concept qui suggère que le processus de la diffusion peut être perçue comme une propagation d'ondes que nous avons

baptisées ondes osmotiques. La similitude entre les équations d'évolution du (c,w)-model avec celles des fluides compressibles nous a permis de mieux comprendre et de réinterpréter les différents comportements de la diffusion. La méthode des caractéristiques nous a, en plus, renseignés sur la possibilité de la formation des discontinuités et de la propagation des ondes non-linéaires. L'utilisation d'un nombre adimensionnel, M_{diff}, qu'on a appelé nombre de Mach de diffusion, permet de classifier les différentes régions de la diffusion. La diffusion Fickienne, obtenue pour des valeurs de M_{diff} plus petites que l'unité, devient la diffusion subosmotique. Le comportement Cas II, obtenu pour des valeurs de M_{diff} plus grandes que l'unité, correspond à la diffusion superosmotique. Dans cet esprit, nous avons aussi étudié la propagation des ondes linéaires pour lesquelles la vitesse de phase ainsi que l'atténuation de l'intensité ont été calculées. Afin de confronter les prédictions du (c,w,m)-model aux observations expérimentales, nous avons fait recours aux méthodes numériques ce qui a nécessité la détermination de l'expression de l'énergie libre. L'expression de Flory est choisie pour la partie exprimant le mixage, et celles de Maxwell et de FENEP sont utilisées pour la partie élastique. Cette dernière a été modifiée d'une manière appropriée pour tenir compte d'un gonflement éventuel du polymère. Comme le gonflement produit aussi un déplacement des frontières, les équations d'évolution ont été reformulées dans les coordonnées Lagrangiennes (description matérielle) en introduisant la matrice de distorsion. L'étude adimensionnelle du modèle (c,w,m)-model, met en évidence l'existence de trois paramètres De, de et K qui représentent l'individualité du mélange étudié. Le premier, De, appelé nombre w-Deborah, est exprimé en fonction du nombre diffusion de Mach, M_{diff}. Le second, de, appelé nombre m-Deborah, mesure l'importance des effets viscoélastiques. Le dernier paramètre, K, est une constante qui couple la diffusion à la structure interne. Un choix approprié de ces trois paramètres qui sont calculés en fonction des propriétés intrinsèques du mélange étudié, permet de décrire un vaste domaine d'observations expérimentales. Les prédictions de ces modèles sont comparées aux résultats expérimentaux pris de la littérature, et un bon accord a été

trouvé. Parmi les résultats obtenus, nous arrivons à expliquer le comportement Cas II sans supposer la transition vitreuse-caoutchouteuse.

La dernière partie de ce travail (Article 5), étend la description du processus de la diffusion d'un seul composant à celle de deux composants dans un polymère. L'intérêt d'une telle investigation apparaît clairement dans plusieurs domaines d'applications industrielles telle que la séparation de phase effectuée par pervaporation, protection contre les mélanges de gaz toxiques etc. Les variables d'état dans ce cas, sont les fractions massiques c_1 et c_2 des deux fluides simples, leurs flux de masse $\mathbf{w}_1$ et $\mathbf{w}_2$ et le tenseur d'ordre deux $\mathbf{m}$ décrivant la structure interne. Le processus de la diffusion est considéré comme un processus avec une triple inertie : l'inertie provenant des deux flux de masse et celle liée à la structure interne $\mathbf{m}$. Dans cette partie, nous avons limité l'analyse à deux cas particuliers i) la diffusion sans inertie qui conduit au modèle de Fick généralisé et ii) la diffusion avec une double inertie qui résulte de la réponse retardée des deux flux de masse $\mathbf{w}_1$ and $\mathbf{w}_2$. Dans le dernier cas, nous avons étudié la possibilité de la propagation des ondes linéaires, et calculé leur vitesse de phase et leur atténuation. Cette étude prédit, dans le domaine des hautes fréquences, la propagation de deux types d'onde ayant des vitesses constantes. Des solutions numériques détaillées sont fournies et comparées avec deux types d'observations expérimentales : i) des mesures obtenues par la pervaporation d'un mélange toluène-benzène par une membrane de polytéréphtalate d'éthyl et ii) des mesures de sorption dans un polymère vitreux d'un mélange de deux solvants, l'un exhibant le comportement Fickien et l'autre le comportement Cas II.

ABSTRACT

Coupling between diffusion and the deformation of the internal structure, observed in solvent-polymer mixtures subjected or not to an applied flow, has been identified as one of the determinant factors that influences the behavior of diffusion, flow and the polymer internal structure. Flow induced phase separation, formation of morphologies, migration across streamlines, etc. are some of the flow-induced behaviors observed in polymer solutions undergoing flow. Moreover, in the absence of flow, measurements collected from the classical experiments of mass transfer (sorption, permeation, pervaporation etc.) show behaviors, called non-Fickean or viscoelastic, that cannot be recovered in terms of the classical and linear Fick's laws. One of the principal reasons for these observations lies in the fact that the most essential properties of polymers are based on the nonlinear and the individual character of the microstructure.

The aim of this work is to understand these effects in both i) binary mixtures consisting of one simple and one complex fluid and ii) ternary mixtures composed of two simple and one complex fluids. We have derived systematically, in the framework of GENERIC (General equation for equilibrium and non-Equilibrium Reversible and Irreversible Couplings), new models capable of describing several observed phenomena that have still remained unexplained by the previously derived models. The governing equations describing the time evolution of the system under consideration are parameterized by the free energy and the relaxation times of the non-conserved state variables. These parameters express all the individual features of the studied mixture.

During the last decade, it has become obvious that for an appropriate description of the dynamical behavior of binary mixtures, the latter has to be regarded as consisting of two fluids each of which is described by its own state variables, that are, in the context of classical hydrodynamics, the mass density ρ_i and the vector linear momentum density $\mathbf{u}_i$ (i designates the fluid i). The state variable characterizing the internal structure, that must

be included into the formulation, is chosen to be the configuration space distribution ψ or its second moment, the conformation second order tensor, $\mathbf{m}$. The set of the state variables for the whole mixture are then obtained via an adequate one-to-one transformation. In case of binary mixtures (see articles 1, 2 et 3), the state variables are the scalar global mass density ρ, the vector linear overall momentum density $\mathbf{u}$, the scalar mass fraction c and the vector relative momentum density $\mathbf{w}$ of one component, and the symmetric second order tensor, $\mathbf{m}$, characterizing the microstructure. For ternary mixtures (see articles 4 and 5), we have extended the concept of the two-fluid model to what we have called the three-fluid model. The set of the state variables include, in addition to those specified for binary mixtures, the scalar mass fraction c_2 and the vector relative momentum density $\mathbf{w}_2$ of the second component.

The equations governing the time evolution for binary (see article 1) and ternary (see article 4) miscible mixtures subjected to an applied flow, show explicitly that the diffusion depends anisotropically on the flow and on the deformation of the microstructure. Reciprocally, the internal structure is influenced by both the external and the internal flows. The latter is produced, of course, by diffusion. In addition to this mutual dependence, elastic stresses are created by relative motions (mass fluxes) within the mixture and consequently modify the dynamical behavior of the flow. In ternary mixture, other new couplings arise among the mass fluxes. In the process of solving asymptotically the governing equations, we have found out that the transport coefficients are functions of the relaxation times and are then expressible in terms of the friction coefficients. Furthermore, in the non linear regime, these coefficients depend explicitly on the gradient of the applied velocity $\kappa_{\alpha\beta} = \partial v_\beta / \partial r_\alpha$ which render the process of diffusion highly anisotropic even in the absence of the internal stresses produced by the internal deformation.

In the absence of an applied flow, coupling between diffusion and deformation engenders new behaviors commonly known as non-Fickean and viscoelastic. Their description requires, in the context of the model derived for flowing mixtures, the

application of the mechanical equilibrium and the global incompressibility constraints. Consequently, the global mass density ρ and the vector overall momentum density $\mathbf{u}$ become dependent state variables and are thus discarded form the set of the state variables.

The non-Fickean diffusion of one solvent in a polymer, in the absence of an external flow, is described by the model, called (c,w,m)-model, in which the inertia of the mass flux and of the conformation are both taken into account. In the process of solving asymptotically the governing equations, we have shown that all the models developed previously in the literature are found as particular cases of the (c,w,m)-model. In this reduction to simpler models, we have arrived at a new model called (c,w)-model in which only the two state variables c and w are sufficient for recovering many nonstandard behaviors, in particular the Case II mass transport, also called the Alfrey' shock wave due to its wave-propagation type. It is regarded as one of the most interesting and striking observation of the non-Fickian diffusion. To explain such a behavior, we have introduced a new concept, that is, diffusion can be regarded as a propagation of osmotic waves . The apparent similarity between the governing equations of the (c,w)-model and those derived in the context of compressible fluid mechanics allows us to better understand and to reinterpret the different behaviors. The characteristic method provides an information about possible formation of discontinuities and propagation of non linear waves. To classify the different regions of the mass transport, a dimensionless number, M_{diff}, called a diffusion Mach number is introduced. Fickian diffusion becomes subosmotic and is recovered if M_{diff} is lower than unit. Case II is a superosmotic behavior and corresponds to M_{diff} greater than unit. On the same footing, we have investigated the propagation of linear waves for which analytical formulas are provided for both the phase velocity and the attenuation. In order to compare the predictions of the (c,w)-model and of the (c,w,m)-model with results of experimental observations, we resort to numerical solutions. For the numerical analysis, we have to specify the free energy. We make two choices : the Maxwell free energy and the FENEP free energy. Both are appropriately modified to take into account the

swelling of the polymer. During swelling, the boundaries of the polymer move and the boundary conditions need to be adequately re-specified during the penetration. To overcome this difficulty, we reformulate the governing equations in the Lagrangean (material) coordinates by using the deformation matrix. The dimensionless governing equations of the (c,**w**,**m**)-model involve three parameters De, de and K. The first, De, called **w**-Deborah number is expressed in terms of the diffusion Mach number M_{diff}. The second, de, called **m**-Deborah number is a kind of viscoelastic Deborah number. We recall that the Deborah number compares the relaxation characteristic time scale of the material to the diffusion characteristic time scale. The third parameter, K, is an indicator of the coupling arising between diffusion and the internal structure. With an appropriate choice of these parameters, we reproduce results of several observations selected from the literature. The prediction of these models are compared with the measurements of a sorption experiment and a rather good agreement was found. More importantly, we were able to recover the Case II behavior without assuming the glass-rubber transition.

Finally, in the last part of this work (see article 5), we generalize the model developed for the penetration process of one component to two components into a polymer. The models derived here are suitable for describing processes of industrial importance, i.e. separation by pervaporation, sorption or permeation through glassy polymers, protection against toxic gas mixtures, drug delivery systems. The state variables are two scalars representing the mass fractions c_1 and c_2 of the two simple fluids, two vectors representing their relative momentum densities $\mathbf{w}_1$ and $\mathbf{w}_2$, and a second order tensor, **m**, characterizing the internal structure of the polymer. Diffusion becomes a process with triple inertia : inertia of the two mass fluxes $\mathbf{w}_1$ and $\mathbf{w}_2$ and the inertia of the internal structure deformation **m**. In this part, we concentrate, the analysis, on diffusion i) without inertia that leads to a generalized Fickean model and ii) with a double inertia stemming form $\mathbf{w}_1$ and $\mathbf{w}_2$. Analytical development for the propagation of linear waves is provided for the latter case and formulas for the phase velocity and the attenuation are calculated. In the high frequency limit, the model predicts the propagation of two types of waves with a constant velocity. Detailed numerical solutions

are found and compared with results of two types of experimental observations: (i) measurements of the pervaporation process of toluene-benzene mixture by a poly(ethylene terephthalate) rubbery membrane, and (ii) measurements of sorption profiles in a mixture of two solvents, one exhibiting the Fickian diffusion and the other the Case II diffusion, penetrating a glassy polymer.

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Symboles Latins

A	matrice
A	fonction arbitraire
B	fonction arbitraire
c_i	fraction massique du composant i
c	fraction massique du solvant
D	matrice des coefficients de diffusion
D	coefficient de diffusion
D_{ij}	éléments de la matrice des coefficients de diffusion
F	matrice de déformation
G	module d'élasticité
i	nombre complexe ($i^2=-1$)
J_i	vecteur flux de masse du composant i
k	vecteur d'onde
L_o	épaisseur initiale de l'échantillon
m	tenseur de conformation
M_i	poids moléculaire du composant i
M	quantité de solvant absorbée par le polymère
N_A	nombre d'Avogadro
N	nombre de particules
P	pression osmotique du gonflement
r	vecteur position eulerienne
R	constante des gaz
t	temps
T	température thermodynamique

$\mathbf{u}$	vecteur densité de la quantité de mouvement globale
$\mathbf{u}_i$	vecteur densité de la quantité de mouvement du composant i
v_{ph}	vitesse de phase
V	volume
$\mathbf{w}$	vecteur densité de la quantité de mouvement relative
$\mathbf{w}_i$	vecteur densité de la quantité de mouvement relative du composant i
v_i	vitesse du composant i
$\overline{V}_1$	volume molaire du solvant
$\mathbf{Y}$	vecteur position dans les coordonnées Lagrangiennes

Symboles Grecques

α	atténuation
ω	fréquence des ondes planes
ϕ	fraction volumique du solvant
φ	densité de l'énergie libre
μ	potentiel chimique
η	viscosité
ρ	densité de masse
σ	tenseur de contrainte
τ	temps de relaxation
Λ	paramètre phénoménologique
ε	tenseur de déformation
ψ	fonction de distribution de l'espace de configuration
Ψ	potentiel de dissipation
Φ	energie libre de Helmholtz
η	tenseur viscosité du mélange binaire
π_i	pression osmotique du composant i

Chapitre 1. Introduction

Depuis que la communauté scientifique s'est penchée sur l'étude des polymères, d'indispensables applications industrielles ont été mises à jour exploitant les comportements intéressants de ces systèmes. D'ailleurs, l'intérêt pour ces matériaux insolites ne cesse, aujourd'hui, de croître comme le prouvent les diverses et nombreuses études consacrées à l'investigation de leurs propriétés physico-chimiques et de leurs comportements. Dictés essentiellement par le caractère d'individualité et de la non-linéarité de la microstructure, ces comportements deviennent généralement inexplicables quand on essai de leur appliquer les théories développées jadis pour les matériaux standards. Bien évidemment, la diffusion de la matière est un processus qui ne s'exclut pas de cette règle. En effet, il est devenu actuellement irréfutable que les lois de Fick sont incapables de reproduire correctement les mesures obtenues à l'aide des expériences classiques de diffusion (sorption, perméation, désorption, pervaporation, etc.) d'un ou de plusieurs solvants dans un polymère. Parmi les raisons mises en cause dans de telles déviations, on identifie principalement les couplages entre la diffusion et la déformation de la structure interne, qui se révèlent être très importants pour influer sur leurs comportements respectifs. L'effet de ces couplages ne se limite pas uniquement aux mélanges en équilibre mécanique, mais il a été aussi détecté dans les mélanges soumis à un écoulement externe. Actuellement, on peut distinguer deux domaines où des observations expérimentales impliquent ces couplages.

i) La rhéologie des systèmes homogènes a montré, à maintes reprises, qu'un cisaillement simple induit dans les solutions semi-diluées de polymères des changements de la structure telles que la séparation de phase, la formation de nouvelles morphologies, la précipitation, etc.

ii) La diffusion de solvants dans les polymères vitreux exhibe généralement un comportement non standard, qualifié de non-Fickien, tels que le transport Cas II (Case II), la sorption sigmoïde, la diffusion pseudo fickienne, la sorption en deux étapes etc.

Ces observations restèrent incompréhensibles et inexpliquées jusqu'à ce que, l'effet de ces couplages ait été tenu en considération. Dans le premier cas, la déformation de la structure interne est produite simultanément par deux types d'écoulement : l'un est imposé par l'extérieur (application d'une force ou d'un couple), et l'autre, de type de diffusion, est généré intérieurement par suite des inhomogénéités spatiales. Dans le second cas, la déformation est produite uniquement par l'écoulement interne dû au gradient de la force active (diffusion chimique).

On relie essentiellement ces comportements à la réponse retardée du milieu, qui modifie le déplacement des particules du solvant en les déviant de leurs mouvements aléatoires brownien (ou Fickien). En effet, contrairement aux milieux Fickiens, le temps de relaxation de la microstructure dans les milieux non-Fickiens devient comparable ou plus grand que le temps caractéristique de la diffusion. Dans cette échelle de temps, la diffusion, devient tributaire du comportement rhéologique du polymère et de l'inertie des flux de masse. Réciproquement, l'évolution de la structure interne et celle de l'écoulement sont modifiées par la présence de mouvements relatifs additionnels crées par les flux de diffusion des différentes composantes. L'amplitude de ces flux peut devenir, dans certains cas, significative pour engendrer des inhomogénéités spatiales et des contraintes internes qui influent sur la nature rhéologique du polymère.

Il est indéniable qu'il devienne nécessaire de comprendre l'importance de ces couplages et leurs influences sur les processus de la diffusion et de l'écoulement à la fois sur le plan fondamental et du point de vue pragmatique, tout particulièrement pour les nouvelles applications industrielles qui en découlent. On peut citer de manière non-exhaustive, la séparation de phase produite par écoulement ou par pervaporation, la libération contrôlée et ciblée des médicaments, le séchage, la protection, etc.

Le travail de la thèse porte sur l'étude des comportements non standards de la diffusion d'un et de deux solvants dans les polymères en présence ou non d'un écoulement externe. On met particulièrement en évidence l'importance des couplages qui surviennent entre l'écoulement (externe et ou interne) et la déformation de la structure interne.

Le plan de la thèse sera organisé comme suit :

- Le deuxième chapitre est consacré à une revue bibliographique. Etant donné que les articles sont relativement détaillés, ce chapitre sera relativement concis et bref afin d'éviter la redondance.
- Le troisième chapitre porte sur l'objectif du travail entrepris et le lien entre les articles.
- Le quatrième chapitre discute l'importance du couplage entre la rhéologie et la diffusion dans les mélanges binaires. Pour une description systématique, nous avons tout d'abord étudié les mélanges composés de deux fluides simples et ensuite les mélanges composés d'un fluide simple (e. g. solvant) et d'un fluide complexe (e. g. polymère).
- Le cinquième et le sixième chapitres modélisent les comportement de la diffusion non-Fickienne en l'absence d'un écoulement externe en tenant compte de la réponse retardée du flux de masse et de la déformation de la structure interne du polymère.
- Le septième chapitre est une généralisation directe du quatrième chapitre. Nous avons introduit le modèle à trois fluides (three-fluid model) qui généralise l'idée du modèle à deux fluides (two-fluid model). Le système ternaire étudié est composé de deux fluides simples (e. g. solvants) et d'un fluide complexe (e. g. polymère).
- Le huitième chapitre étend le travail du cinquième chapitre pour discuter les processus de la diffusion de deux fluides simples dans un polymère. Cette étude est particulièrement utile pour comprendre, entre autres, le processus de la séparation entre les composants d'un mélange par pervaporation, la protection contre un mélange de gaz, etc.

- La conclusion et les recommandations constituent le dernier chapitre pour clore ce travail.

Chapitre 2. Revue bibliographique

2.1. Introduction

Depuis que des expériences effectuées sur des systèmes binaires composés d'un fluide simple et d'un polymère soumis ou non à un écoulement externe, ont montré que la diffusion et la déformation de la structure interne sont étroitement liées, il est devenu inéluctable qu'il faille tenir compte de leur dépendance mutuelle dans la modélisation.

Plusieurs auteurs ont essayé d'introduire les effets de ces couplage de manière ad hoc pour expliquer les observations qui sont restées réfractaires aux prédictions des théories classiques basées sur l'idée d'un fluide unique. Ces tentatives restèrent, toutefois incomplètes et insatisfaisantes jusqu'à l'apparition des modèles basés sur l'idée de deux fluides (two-fluid model) qui a constitué le point tournant dans la compréhension de l'influence de ces couplages sur les comportements de l'écoulement, de la diffusion et de la structure interne. En s'inspirant de la théorie de Landau qui avait été le premier à avoir utilisé le concept de deux fluides pour expliquer le caractère superfluide de l'Helium, De Gennes (1976) l'a appliqué aux milieux continus. Comme son nom l'indique, ce modèle considère que chaque fluide, dans le mélange binaire, est décrit par ses propre variables d'état. Grâce à cette idée simple, le couplage entre la déformation de la structure interne et la diffusion devient explicitement exprimable dans la formulation théorique. En effet, il suffit de considérer comme point de départ les équations d'Euler correspondant à chaque fluide, de les transformer via une transformation biunivoque appropriée, pour aboutir à des équations pour le mélange qui couplent naturellement la diffusion, la déformation et l'écoulement. Durant la dernière décennie, ce concept a préludé au développement de plusieurs théories dynamiques pour les mélanges binaires qui mettent en évidence

l'importance des mouvements relatifs internes (flux de diffusion). Ces derniers se créent au sein du système global par la présence de différents composants qui se déplacent avec leurs propres vitesses. Cependant, ce n'est guère qu' avec l'apparition du formalisme GENERIC (Grmela et Ottinger 1997) que l'importance des couplages précités est devenue relativement simple et explicite dans une formulation dynamique pour les systèmes binaires et ternaires. Cette méthode Hamiltonienne appliquée aux milieux continus est longuement présentée dans les chapitres suivants. Elle a été développée pour garantir la compatibilité avec la thermodynamique, et notamment pour assurer qu'en l'absence de forces extérieures, le système évolue vers un état final d'équilibre thermodynamique.

Ce chapitre sera organisé comme suit. La section 2.2 discutera brièvement les lois de Fick, leurs prédictions aphysiques et leurs extensions dans le cadre de la thermodynamique hors équilibre. La diffusion non-fickienne dans les systèmes binaires et ternaires fait l'objet du second paragraphe, 2.3. Le dernier paragraphe, 2.4., est consacré au couplage entre la rhéologie et la diffusion.

2.2. Théories classiques de la diffusion

2.2.1. Systèmes binaires : Lois de Fick et leurs prédictions aphysiques

Les deux lois proposées par Fick en (1885) décrivent relativement bien la diffusion des petites molécules dans les substances simples tels que les gaz, les liquides et les solides. Par substance simple, on comprend un milieu dont la structure interne évolue dans une échelle de temps très différente (très petite ou très grande) de celle du temps caractéristique de la diffusion et par conséquent, ne peut influencer le processus du transfert de masse. La première loi de Fick stipule que, localement, le vecteur densité du flux de masse $\mathbf{J}(r,t)$ de la quantité diffusant dans un milieu binaire simple, est proportionnel à son gradient de concentration $c(r,t)$

$$\mathbf{J}(\mathbf{r},t) = -\rho D\ \nabla c(\mathbf{r},t) \tag{2.1}$$

où ρ est la densité globale du mélange binaire (masse par unité de volume). D est le coefficient *constant* de diffusion mutuelle (m^2/s). La deuxième loi de Fick, qui découle naturellement de l' équations de continuité , s'écrit sous la forme

$$\rho\frac{\partial c}{\partial t} = -\partial_\alpha J_\alpha \tag{2.2}$$

où le symbole $\partial_\alpha = \partial/\partial r_\alpha$ désigne la dérivée spatiale. Si on substitue l'expression (2.1) dans l'équation (2.2) on obtient l'équation parabolique suivante

$$\frac{\partial c}{\partial t} = D\nabla^2 c(\mathbf{r},t) \tag{2.3}$$

∇^2 est le Laplacien. Outre sa simplicité, la théorie de Fick permet de décrire aussi bien qualitativement que quantitativement la diffusion dans les milieux binaires simples. Notons que du point de vue de la thermodynamique, la concentration c constitue alors la seule variable d'état qui permet de décrire complètement le transfert de masse d'une région de l'espace vers une autre. Des solutions assez détaillées de l'équation (2.3) pour plusieurs géométries et différentes conditions initiales et de frontières, peuvent être trouvées, par exemple, dans le livre de Crank (1975).

2.2.1.a. Modèle de Fick : ses prédictions aphysiques et son extension par la méthode de la thermodynamique hors équilibre.

En étudiant les phénomènes de la propagation de la chaleur, Cattaneo s'était rendu compte que l'équation parabolique qui découle de la loi de Fourier prédit aux hautes fréquences, une vitesse de propagation infinie. Pour remédier à cette situation

physiquement inadmissible, un terme exprimant la relaxation du flux de la chaleur est ajouté dans l'équation de Fourier (Jou et al. 1984, 1993). D'une manière générale, toute loi décrivant la propagation d'une grandeur physique et exprimée sous la forme de la loi de Fourier présenterait les mêmes anomalies physiques aux hautes fréquences. Cela n'exclut pas évidemment la théorie parabolique de Fick décrite par les équations (2.1)-(2.3). Pour tenir compte de l'inertie du flux de masse J (Jou et al. 1984, 1993), l'équation (2.1) a été reformulée dans le même esprit que celui adopté pour le transfert de la chaleur,

$$\tau\frac{\partial \mathbf{J}}{\partial t} = -\rho D\,\nabla c - \mathbf{J} \qquad (2.4)$$

τ est le temps de relaxation. Pour de faibles valeurs de τ, l'équation (2.4) coïncide avec la première loi de Fick donnée par (2.1). Cette extension, dans laquelle le flux de masse est considéré comme une variable d'état additionnelle, constitue la tendance actuelle des méthodes de la thermodynamique irréversible étendue (EIT : Extended Irreversible Thermodynamics) (Jou 1993). Combinant (2.2) et (2.4), on arrive à

$$\tau\frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} - D\Delta c = 0 \qquad (2.5)$$

qui est connue sous le nom de l'équation télégraphique. Cherchant les solutions de l'équation (2.5) sous forme d'ondes planes unidimensionnelles

$$c = c_0 \exp[i(kx - \omega t)] \qquad (2.6)$$

ω est la fréquence de l'onde, k est le nombre d'onde et c_0 est son amplitude. La relation de dispersion obtenue par substitution de (2.6) dans (2.5) est de la forme

$$\omega^2 + \left(\frac{i}{\tau}\right)\omega - \left(\frac{D}{\tau}\right)k^2 = 0 \qquad (2.7)$$

Il en résulte que la vitesse de phase et la distance d'atténuation sont

$$v_{ph} = \frac{\omega}{\mathrm{Re}\, k} = \frac{\sqrt{2D\omega}}{\sqrt{\tau\omega + \sqrt{1+\tau^2\omega^2}}} \qquad (2.8)$$

et

$$\alpha(\omega) = \frac{1}{\mathrm{Im}\, k} = \frac{2D}{v_{ph}} \qquad (2.9)$$

Aux basses fréquences ($\omega \ll 1$), $v_{ph} = \sqrt{2D\omega}$ et $\alpha = \sqrt{2D/\omega}$ sont les résultats prédits par la théorie classiques de Fick. Aux hautes fréquences ($\omega \gg 1$), $v_{ph\infty} = \sqrt{\frac{D}{\tau}}$ et $\alpha_\infty = 2\sqrt{D\tau}$. Il est intéressant de voir que dans la limite $\tau = 0$, qui correspond à la loi de Fick, on obtient les solutions aphysiques suivantes : $v_{ph\infty} \to \infty$ et $\alpha_\infty = 0$.

En plus de ces prédictions aphysiques, plusieurs observations expérimentales concernant la diffusion dans les polymères vitreux, les gels, les mélanges de polymères, les milieux poreux (Alfrey et al. 1966 ; Barrière 1997 ; Billovits et al. 1993 ; Durning et al. 1995 ; Gall et al. 1990, 1991 ; Hassan et al. 1999 ; Huang et al. 1997; Hui et al. 1987, Kewi et Zupko 1969 ; ; Lasky et al. 1987 ; Long et Richman 1960 ; Thomas et Windle 1978, 1981) viennent infirmer les lois de Fick Malgré la nécessité d'introduire le concept de la réponse retardée du flux de masse, les comportements observés dans ces milieux deviendraient inexplicables si on ne tient pas compte des effets de couplage entre la diffusion et la déformation de la structure interne du polymère. Il est évident qu'exprimer un tel couplage dans le cadre des lois de Fick (2.1)-(2.3), est loin d'être trivial, ce qui

requiert pour leur généralisation l'utilisation de la compatibilité de la diffusion avec la thermodynamique. Dans la section 2.3., on montrera que c'est par le biais de cette compatibilité qu'il est devenu possible de mettre en évidence l'effet d'un tel couplage dans les systèmes binaires en équilibre mécanique (qui ne sont pas soumis à un écoulement externe).

2.3. Diffusion non-Fickienne en l'absence d'un écoulement externe.

2.3.1 Systèmes binaires : couplage diffusion-déformation

La diffusion, qualifiée de non-Fickienne ou viscoélastique, de solvants dans les polymères a été longuement étudiée aussi bien expérimentalement (Alfrey et al. 1966 ; Barrière 1997 ; Billovits et al. 1993 ; Durning et al. 1995 ; Gall et al. 1990, 1991 ; Hassan et al. 1999 ; Huang et al. 1997; Hui et al. 1987, Kewi et Zupko 1969 ; ; Lasky et al. 1987 ; Long et Richman 1960 ; Thomas et Windle 1978, 1981) que théoriquement (Durning 1985 ; Durning et Tabor 1986 ; Edwards et al. 1995 ; Fu et al. 1993 ; Jou et al. 1984, 1993 ; Peppas et al. 1994 ; Thomas et al. 1982; Wu et Peppas, 1993). Généralement, les comportements observés, qui ne sont pas prédictibles par la théorie de Fick, sont reliés aux temps de relaxation très lents que mettent les chaînes pour se réarranger afin de loger les molécules diffusantes. Jusqu'à maintenant, on a pu identifier plusieurs comportements dans les polymères vitreux telles que la sorption sigmoïde, la sorption en deux étapes, la sorption pseudo-Fickienne, etc. Cependant, le cas qui a suscité le plus d'intérêt de la part de la communauté scientifique reste sans aucun doute la diffusion Cas II telle qu'elle a été baptisée par Alfrey et al. (1966). Ce cas se distingue par les caractéristiques suivantes :

(i) la masse absorbée croit linéairement dans le temps.

(ii) Un front abrupt sépare le polymère en une partie vitreuse encore sèche et une partie gonflée dans laquelle il n'y a aucun gradient de concentration.

(iii) Le front du solvant se déplace avec une vitesse constante.

(iv) Le polymère reste dans son état vitreux après le processus de la diffusion.

(v) Il y a souvent un temps d'induction (appelé aussi temps d'incubation) durant lequel le front s'établit à la surface du film.

Alfrey et al. (1966) ont remarqué que les comportements viscoélastiques observés dans les expériences unidimensionnelles de la sorption se rangent entre deux cas limites extrêmes : le transport Cas II décrit ci dessus et la diffusion Fickienne appelée aussi Cas I. Le premier est caractérisé par une vitesse constante et le second par le coefficient de diffusion D constant. Cette classification trouve son origine dans le fait qu'à l'instant initial, la position du front, X, est donnée par la relation expérimentale simple $X = qt^n$ où q est une constante, n est un nombre réel et t représente le temps . D'une manière similaire, la masse par unité de surface de la quantité du solvant absorbée par le polymère, M(t) , peut s'écrire comme $M = qt^n$. Pour le Cas I, n = ½, pour le Cas II n =1 et pour les cas intermédiaires $0.5 < n < 1$. À l'exception du comportement SuperCas II observé ultérieurement et pour lequel n = 2, presque tous les cas non linéaires obtenus par des mesures de sorption ou de perméation se conforment à cette classification.

L'observation, qui date de longtemps, d'un front de solvant raide qui traverse le polymère ne constitue pas une condition suffisante pour prédire le transport Cas II. Dans la majorité des cas où un front visible est détecté, il avance dans le polymère avec une vitesse décroissante. Dans les milieux Fickiens où le front du solvant varie selon la relation $X = qt^{0.5}$, il se déplace avec une vitesse, $dX/dt = \frac{1}{2}qt^{-0.5} = \frac{q^2}{2X}$, qui décroît dans le temps ainsi qu'en fonction de la profondeur de pénétration. En revanche, le transport Cas II, appelé aussi onde de choc d'Alfrey, est caractérisé par un front abrupt qui ne décélère pas. Son observation ne constitue pas un cas isolé, mais elle a été reportée dans plusieurs mélanges tels que le polystyrène dans l'acétone, le polystyrène dans les n-alcanes (Alfrey et al. 1966), la résine d'époxide réticulée dans le benzène (Kwei et Zupko

1969), le polyméthacrylate de méthyle dans le méthanol (Thomas et Windle 1978, 1982) etc.

Les premières tentatives pour expliquer la vitesse constante de ce front, ont été basées sur la théorie de Fick à laquelle de légères modifications ont été apportées. Rappelons qu' initialement, la diffusion Fickienne décrite par les équations (2.1)-(2.3) considère un coefficient de diffusion constant. Et pourtant, même dans les polymères caoutchouteux, le coefficient de diffusion varie avec la concentration du solvant, ce qui requiert l'utilisation de la loi de Fick généralisée

$$\partial c/\partial t = \nabla.[D(c)\nabla c] \qquad (2.10)$$

Afin d'expliquer la vitesse constante du front dans les polymères vitreux, Crank a supposé que le coefficient de diffusion D(c) subit un saut de discontinuité de l'ordre de 100-1000 quand on passe de la région gonflée à la région encore sèche. Avec des conditions initiales et aux frontières normales, il arrive à obtenir, à l'aide de l'équation (2.10), le déplacement d'un front abrupt, qui toutefois, décélère dans le temps. Cette discontinuité dans D suppose que le polymère subit une transition vitreuse-caoutchouteuse, alors que l'expérience montre qu'il reste dans son état vitreux à la fin du processus de la sorption (Alfrey et al. 1966 ; Barrière 1997 ; Thomas et Windle 1978, 1981). Une autre tentative, suggérait un coefficient de diffusion variant dans le temps (Crank 1953).

Plus tard, la relaxation moléculaire des chaînes de polymères fut considérée un facteur essentiel dont il faut tenir compte pour comprendre ces comportements non-Fickiens. Dans ce contexte, l'influence de la microstructure sur la diffusion devrait être explicitement incluse dans les formulations mathématiques. La question qui s'était imposée à l'époque était comment faut-il l'introduire dans ce processus ?. Cette tâche devient ardue dans le cadre de la théorie de Fick ou de sa forme généralisée (2.10). Afin de contourner cette difficulté, le coefficient D a été postulé dépendre exponentiellement

de la concentration et de la contrainte interne du polymère traité alors comme un milieu viscoélastique. Cependant, l'existence du front abrupt se déplaçant avec une vitesse constante était loin d'être reproduite par ces modèles qui, généralement manquent de bases physiques solides pour qu'ils soient considérés comme définitifs pour décrire correctement les observations expérimentales de la diffusion viscoélastique. Toutefois, cette tentative de relier les effets de la relaxation du polymère au processus de la diffusion a pris un nouvel essor, une fois la compatibilité de la diffusion avec la thermodynamique a été utilisée. En effet, comme la concentration est influencée par la relaxation des chaînes du polymère, la force active pour la diffusion devient le gradient du potentiel chimique du solvant plutôt que le gradient de la concentration. Ceci permet d'exprimer le flux du solvant comme

$$\mathbf{J}(\mathbf{r},t) = -\rho D_1 \nabla \mu_1 \tag{2.13}$$

μ_1 est le potentiel chimique du solvant qui dépend de la fraction massique c et de la pression osmotique de gonflement P. En supposant l'incompressibilité matérielle du solvant, les modèles proposés dans la littérature utilisent la fraction volumique ϕ au lieu de la fraction massique. Par application de la règle de dérivation par chaîne, on arrive dans le cas d'une description unidimensionnelle à

$$J = -\rho D_1 \left[\left(\frac{\partial \mu_1}{\partial \phi} \right) \phi_x + \left(\frac{\partial \mu_1}{\partial P} \right) P_x \right] \tag{2.14}$$

où A_x exprime la dérivée spatiale de la quantité A ($A = \phi, P$) par rapport à x choisie ici pour désigner la coordonnée spatiale. Le potentiel chimique du solvant s'écrit sous la forme

$$\mu_1 = \mu_1^0 + RT \ln a_1 + \overline{V}_1 P \tag{2.15}$$

les paramètres μ_1^0 , a_1 et $\overline{V}_1$ sont respectivement le potentiel chimique référence, l'activité et le volume molaire du solvant. R est la constante des gaz et T est la température ambiante. Afin d'introduire l'influence de la structure interne, on utilise la condition de l'équilibre mécanique

$$\frac{\partial P}{\partial x} - \frac{\partial \sigma}{\partial x} = 0 \tag{2.16}$$

qui substituée dans l'équation (2.14) donne

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}\left(D(\phi)\left(\frac{\partial \phi}{\partial x} + \left(\frac{\overline{V}_1}{\mu_{1\phi}} \right) \frac{\partial \sigma}{\partial x} \right) \right) \tag{2.17}$$

où $D(\phi) = D_1 \mu_{1\phi}$. Le transfert de masse est décrit dans ce contexte par les deux variables d'état qui sont la fraction volumique du solvant ϕ et la contrainte interne σ crée dans le polymère par la diffusion. Remarquons que cette dernière variable d'état constitue, en fait, un choix indirect pour décrire la structure interne. On verra dans les chapitres qui suivront que la fonction de distribution de l'espace de configuration ψ ou le tenseur de conformation $\mathbf{m}$ du polymère peuvent constituer des variables d'état alternatives qui ont l'avantage de fournir une description directe de l'évolution de la structure interne. Pour compléter la description donnée par (2.17), une équation d'évolution pour la contrainte est alors ajoutée. Thomas et Windle ont en 1980 supposé que le polymère est purement visqueux et peut ainsi être décrit par la loi de Newton mais avec une viscosité dépendant de la concentration

$$\sigma = \eta(\phi)\frac{\partial \varepsilon}{\partial t} = \eta(\phi)\frac{\partial \phi}{\partial t} \tag{2.18}$$

Substituant (2.16) dans le seconde loi de Fick (2.2), ils arrivent à

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}\left(D(\phi)\left(\frac{\partial \phi}{\partial x} + \left(\frac{\overline{V}_1}{\mu_{1\phi}} \right) \frac{\partial}{\partial x}\left(\eta(\phi)\frac{\partial \phi}{\partial t} \right) \right) \right) \tag{2.19}$$

En vue de retrouver leurs résultats expérimentaux, ces auteurs ont en plus exigé que le coefficient de diffusion doit croître et que la viscosité doit décroître exponentiellement avec la fraction volumique: $D(\phi) = D_0 e^{a\phi}$ et $\eta(\phi) = \eta_0 e^{-b\phi}$, a et b sont des constantes ajustables qui dépendent de la nature du matériau étudié et D_o et η_o sont les valeurs obtenues à la concentration zéro.

La théorie de Thomas et Windle est considérée comme la première formulation qui a introduit explicitement l'effet de la structure interne pour expliquer la diffusion non-Fickienne. Malgré qu'elle ne traite que la diffusion visqueuse, ils l'ont appliquée aux polymères vitreux, ce qui laisse supposer que les chaînes répondent instantanément à la diffusion contrairement avec l'idée d'une relaxation lente des chaînes vitreuses. Pour remédier à cette faiblesse, Durning et Tabor en 1986 ont introduit les effets de la relaxation de la structure interne. Le modèle linéaire de Maxwell a alors été choisi comme modèle rhéologique pour combiner les effets de la réponse instantanée et retardée.

$$\tau_r \frac{\partial \sigma}{\partial t} + \sigma = \eta(\phi)\frac{\partial \phi}{\partial t} \tag{2.20}$$

$\tau_r = \frac{\eta}{G}$ est le temps de relaxation et G est le module d'élasticité. Le transfert de masse acquiert alors sa dénomination de la diffusion viscoélastique. De même, le coefficient de

diffusion et la viscosité doivent, dépendre de la concentration afin d'obtenir un front abrupt du solvant. Plusieurs études mathématiques (Edwards 1995) développées pour ces modèles ont été proposées pour expliquer le comportement onde de choc du transport Cas II.

Généralement, le polymère subit, à cause de la pénétration, des changements de volume (gonflement) qui peuvent être significatifs, surtout s'il présente les propriétés d'élasticité et de l'affinité avec le solvant. L'augmentation du volume du polymère entraîne le déplacement de ses frontières et nécessite par conséquent une connaissance supplémentaire de l'évolution temporelle des conditions aux frontières. Mentionons que cet effet du gonflement du polymère n'apparaît pas clairement dans les équations d'évolution (2.17)-(2.20). Afin de contourner cette difficulté, qui apparaît particulièrement dans la description Eulerienne, il devient plus approprié de reformuler les équations d'évolution dans la description matérielle (Lagrangienne). En mécanique des milieux déformables, on utilise le tenseur gradient de déformation **F** pour relier les coordonnées déformées **r** ou Eulèriennes aux coordonnées non-déformées **Y** ou Lagrangiennes

$$\mathbf{dr} = \mathbf{F}\,\mathbf{dY} \tag{2.21}$$

À une dimension, Wu et Peppas (1993) ont réécrit les équations d'évolution (2.19) dans ce contexte

$$\frac{\partial \phi}{\partial t} = F_{11}^{-1}\frac{\partial}{\partial Y}\left(D(\phi)\left(F_{11}^{-1}\frac{\partial \phi}{\partial Y} + \left(\frac{\overline{V}_1}{\mu_{1\phi}}\right)F_{11}^{-1}\frac{\partial \sigma}{\partial Y}\right)\right) \tag{2.22}$$

Ils ont obtenu dans le régime linéaire

$$F_{11} = \frac{1}{1-\phi} \tag{2.23}$$

et que la quantité de masse par unité de surface du solvant sorbée par le polymère dans le cas d'une expérience de sorption unidimensionnelle se transforme comme

$$\frac{M_t}{M_{eq}} = \frac{\int_0^{L_0} \phi F_{11} dY}{\phi_{eq} F_{11,eq} L_0} \qquad (2.24)$$

M_{eq} est la quantité de solvant absorbée à l'équilibre. Ces travaux résument les grandes tendances des théories développées pour expliquer la diffusion viscoélastique.

Dans la même époque que celle correspondant aux débuts des développements des théories viscoélastiques de la diffusion, Neogi (1983) a indépendamment utilisé, l'équation du flux (2.4) pour expliquer la diffusion Cas II. Cette équation linéaire prédit la propagation d'ondes planes linéaires qui correspond à un comportement, en apparence, similaire à celui du transport Cas II. Cependant, l'absence de la contribution de la déformation de la structure interne ainsi que le caractère linéaire de ses équations a fait que son modèle n'a pas trouvé un écho considérable. En effet, par analogie avec la propagation des discontinuités dans les fluides compressibles (onde de choc, ondes de raréfaction, etc.) qui est un phénomène non-linéaire, la diffusion Cas II ne peut être décrite par les équations de type (2.2) et (2.4) qu'à la condition de les étendre par des termes non-linéaires de convection de flux comme il va être démontré dans le cinquième et sixième chapitres.

2.3.2 Systèmes Ternaires : Lois de Fick Généralisées.

La première loi de Fick (2.1), qui a été développée dans le même esprit que celui des lois linéaires expérimentales de Newton et de Fourier, stipule que dans les milieux binaires isotropes, le flux de masse d'une composante est proportionnel au gradient de sa concentration. Toutefois, toutes les observations expérimentales liées aux phénomènes de

transport ne se conforment pas à de simples relations linéaires entre un flux et une force. En effet, quand deux processus de transport, ou plus, prennent place simultanément dans un milieu, ils peuvent interférer et produire des effets de couplage. Un exemple bien connu est fourni par l'interférence entre la diffusion et la conduction de la chaleur qui donne naissance à l'effet Soret et à l'effet Dufour. Le premier, appelé aussi diffusion thermique, crée un gradient de concentration par application d'un gradient de la température. Le second est l'apparition d'une différence de température survenant par application d'un gradient de concentration. Nous avons déjà vu que la diffusion non-Fickienne d'un fluide simple dans un polymère n'est compréhensible que dans le cadre d'un couplage entre la déformation de la structure interne et le transfert de masse.

Dans les systèmes ternaires, l'interférence entre les flux de masse des différents composants engendre des couplages qui contribuent à la déviation par rapport aux lois de Fick (Ball et al. 2000 ; Cao et al. 1999 ; George et al. 2000 ; Lau et al. 1991 ; Nguyen et al. 2000 ; Suzuki et al. 1982, 1983 ; Uragami et al. 1999). Ces couplages peuvent produire des effets d'entraînement, surtout en présence d'un fort gonflement, où dans le cas de solvants compatibles qui s'entraînent les uns les autres par augmentation du volume libre dans le polymère. Généralement, il est difficile de prédire le comportement de la diffusion pour un mélange par la simple connaissance des comportements des éléments purs qui le constituent (Ball et al. 2000 ; Cao et al. 1999 ; George et al. 2000 ; Lau et al. 1991 ; Nguyen et al. 2000 ; Suzuki et al. 1982, 1983 ; Uragami et al. 1999). Par exemple, dans un même polymère vitreux, la diffusion de certains solvants peut exhiber le comportement Cas II alors que pour d'autres, le comportement est Fickien. La sorption de leur mélange présente un comportement intermédiaire entre les deux cas ci dessus (Kwei et Zupko 1969).

L' étude de la diffusion dans un mélange ternaire constitue l'étape naturelle, après celle consacrée à un mélange binaire, pour comprendre les mélanges à plusieurs composantes qui présentent un intérêt d'évidence fondamentale dans le domaine industriel. Cependant, comme nous allons le voir dans cette section et dans les chapitres

sept et huit, la description dynamique des systèmes ternaires est loin d'être facile et sa généralisation à des systèmes à plusieurs composantes le sera encore moins. Aujourd'hui, le processus de la diffusion d'un fluide simple dans un polymère est relativement bien compris dans le cadre du couplage entre la diffusion et la déformation de la structure interne. Malgré les applications industrielles importantes qu'implique l'utilisation des mélanges ternaires, la description de la dynamique du transfert de masse dans ces systèmes trébuche (Meuleman et al. 1999 ; Zielinski et al. 1999) encore et seules les lois généralisées simples de Fick sont encore utilisées

$$J_1 = -\rho D_{11}\nabla c_1 - \rho D_{12}\nabla c_2$$
$$J_2 = -\rho D_{21}\nabla c_1 - \rho D_{22}\nabla c_2 \qquad (2.25)$$

Soulignons que le système ternaire est considéré comme le système le plus simple pour lequel les relations de réciprocité d'Onsager (de Groot et Mazur 1962 ; Fitts 1962) jouent un rôle très important. Pour un système de n composantes, le nombre de coefficients de diffusion D_{ij} est $(n-1)^2$. D_{ii} sont les coefficients de diffusion principaux et D_{ij} $(i\neq j)$ sont les coefficients de diffusion croisés. Les relations d' Onsager soumettent le système à certaines contraintes qui réduisent le nombre de coefficients de diffusion à $n(n-1)/2$ termes indépendants. Les lois (2.25) peuvent être utilisées pour expliquer le comportement de la diffusion dans les polymère qui ne gonflent pas ou qui gonflent peu (Ball et al. 2000 ; Cao et al. 1999 ; George et al. 2000 ; Lau et al. 1991 ; Nguyen et al. 2000 ; Suzuki et al. 1982, 1983 ; Uragami et al. 1999). Néanmoins, elles restent insuffisantes pour satisfaire plusieurs manifestations expérimentales en particulier celles observées dans les polymères vitreux ou dans les gels. Cependant, due à l'absence de théories similaires à celles développées pour les mélanges binaires, ces lois sont encore utilisées pour expliquer les mesures de la pervaporation d'un mélange par une membrane homogène dense. Rappelons que la pervaporation (Ball et al. 2000 ; Cao et al. 1999 ; George et al. 2000 ; Lau et al. 1991 ; Nguyen et al. 2000 ; Suzuki et al. 1982,

1983 ; Uragami et al. 1999) est une technique de séparation qui a été observée pour la première fois par Kahlenberg (1906) pour des mélanges d'hydrocarbures et d'alcool. Cependant, elle n'a reçu sa dénomination définitive qu'en 1917 par Kober. Elle est considérée comme une technique complémentaire à la distillation pour la séparation entre deux substances qui ont des points d'ébullition très proches ou des mélanges azéotropes. Elle est basée sur l'utilisation d'une membrane dense homogène qui sépare deux compartiments : amont et aval. Le compartiment amont contient le mélange à séparer (appelé aussi la charge) et le compartiment aval est mis sous vide à l'aide d'un système de pompage. Le mélange qui traverse la membrane, sous forme de vapeur, ayant une composition différente de la charge, arrive dans la partie avale où il est collecté à l'aide d'un condenseur. La séparation entre les constituants s'effectue selon deux processus complémentaires i) la sorption inégale à la face amont au contact avec le liquide qui se fait par modification de la composition du mélange qui franchit l'interface charge-membrane dans la partie amont ii) la mobilité différente et inégale des espèces dans le matériau (diffusivité). Cette dernière condition requiert des membranes d'épaisseurs très faibles (quelques microns) pour assurer des application rentables industriellement. Finalement, c'est à partir de 1982 que la technique de pervaporation va être utilisée industriellement pour déshydrater l'éthanol par la firme allemande GFT (Gesellschaft fur Trenntechnik). Cette même année, le premier workshop international portant sur cette méthode s'est déroulé à Nancy (Clément 2000).

2.3.3 Remarques

Si dans les systèmes binaires, la concentration c d'un composant représente la seule variable d'état nécessaire pour décrire via la théorie de Fick le processus de la diffusion dans les mélanges simples, elle devient néanmoins insuffisante pour rendre compte des différents comportements observés. Les effets de la relaxation de la microstructure du polymère a conduit au développement de nouveaux modèles pour esquels l'ensembles des variables d'états est étendu. Les modèles de la diffusion

viscoélastiques, introduisent deux variables d'états qui sont la concentration c et la contrainte σ pour caractériser la structure interne (Durning et Tabor 1986 ; Edwards et al. 1995; Thomas et al. 1982; Wu et Peppas 1993). Le modèle de la thermodynamique hors équilibre de Neogi (1983) utilise deux variables d'états qui sont la concentration c et le flux de masse J.

Les premiers décrits par c et σ requièrent la compatibilité avec la thermodynamique pour introduire les effets de la relaxation, et seule la viscoélasticité linéaire est utilisée. Ces modèles restent cependant limités pour décrire les comportements non linéaires observés dans les polymères qui gonflent et donc passent d'un état d'équilibre initial vers un état d'équilibre final différent. Cette non linéarité apparaît plus particulièrement dans le transport Cas II où les profils de la concentration, de flux de masse et de la conformation sont raides et leurs gradients sont importants pour être négligés. En plus d'ignorer les effets de la réponse retardée du flux de masse, ces modèles exigent un coefficient de diffusion et un coefficient de viscosité qui dépendent fortement de la concentration, contrairement avec certaines observations expérimentales qui montrent que le polymère reste dans son état vitreux à la fin du processus de la sorption.

Le modèle de Neogi (1983), basée sur les concept de la thermodynamique hors équilibre, en plus d'être linéaire, néglige complètement les effets de la déformation du polymère. Dans les polymères élastiques, c'est plutôt la réponse retardée de la déformation qui joue un rôle dominant.

Dans les systèmes ternaires, Il n'y a pas actuellement une description viscoélastique qui tient compte des effets de la microstructure du polymère et de son influence sur la diffusion. A cette lacune, nous avons remédié dans l'article 5.

2.4. Couplage entre la Rhéologie et la Diffusion : Écoulement Externe.

Depuis plus de 40 ans, plusieurs observations expérimentales (Rangel-Nafaile et al. 1984 ainsi que d'autres références citées par ces auteurs) montrent que des

changements de phase peuvent survenir dans les solutions solvant-polymère auxquelles un écoulement est appliqué. De tels comportements induits par écoulement, comme les qualifie la littérature, sont similaires aux transformations qui se produisent, à l'état statique, par un changement de la température (chauffage, refroidissement), et incluent la turbidité, la formation de fibres solides, la cristallisation, la précipitation. Pour examiner ces phénomènes, plusieurs techniques expérimentales ont été utilisées comme la diffusion de la lumière, des rayons X, et des neutrons et qui ont permis de déterminer l'échelle de la longueur caractéristique à partir de laquelle la miscibilité ou la séparation se produisent.

Il est plus aisé de concevoir que sous l'effet de l'écoulement, c'est plutôt la miscibilité qui est favorisée dans les fluides polymériques que la séparation de phase. Toutefois, ce dernier phénomène, plus complexe à décrire que le premier, est observé comme un comportement qui peut être induit par application d'un écoulement externe. Le mélange polystyrène/polyether méthyle de vinyle (PS/PVME) montre une séparation de phase induite par écoulement à des températures en dessous de la température critique LCST (lower critical solution température), mais présente aussi un effet de mélange à des températures supérieures à la LCST. Ces observations, qui sembleraient à première vue contradictoires, compliquent la nature du problème. Cependant, si la tendance pour la miscibilité existe toujours dans les mélanges sous cisaillement, celle pour la séparation semble ne se produire qu'au voisinage de la température critique et surtout quand les deux composants ont des propriétés viscoélastiques très différentes. Les systèmes les plus simples, où ce phénomène survient, sont les solutions formées d'un polymère et d'un solvant. Généralement, cet effet est reporté dans les solutions semi-diluées (Kume et al. 1997 ; Murase et al. 1995), mais même les solutions diluées peuvent l'exhiber dans des géométries d'écoulement curvilignes.

Dans les solutions semi-diluées de polymères, la formation de structures solides correspond à une augmentation de la température de précipitation de plusieurs dizaines de degrés Celsius. Par exemple, les solutions de polystyrène de hauts poids moléculaires

(210^6) dans le phtalate de dioctyle (PS/DOP) deviennent turbides à des températures plus grandes que la température spinodale correspondant à une solution au repos. Rangel-Nafail et al. (1984) ont observé des changements de température de l'ordre de 3 - 28 °C et ont montré que la séparation de phase est sensible à la température, au poids moléculaire et à la fraction volumique du polymère, et au taux de cisaillement. En revanche, elle devient insignifiante et difficilement observable si la fraction volumique du polymère est proche de sa valeur critique et que son poids moléculaire est modéré.

Plusieurs auteurs ont développé des modèles théoriques pour expliquer ces comportements induits par écoulement. On peut citer à titre d'exemples l'utilisation de l'approche pseudo thermodynamique (Rangel-Nafaile et al. 1984; Wolf 1984), la thermodynamique hors équilibre (Doi 1990 ; Helfand 1989 ; Ji 1995 ; LHuillier 1985, 2000 ; Onuki 1989, 1997 ; van Egmond 1997, 1992) et la méthode Hamiltonienne (Beris et Edwards 1994 ; Mavrantzas et Beris 1992) etc.

Rangel-Nafaile et al. (1984) et Wolf (1984), ont modifié l'énergie de Flory-Huggins (1953), φ^{F-H}, qui décrit le mélange statique d'un solvant et d'un polymère en ajoutant un nouveau terme d'écoulement qui est proportionnel à la trace du tenseur de la contrainte mécanique σ^M

$$\varphi = \varphi^{F-H} + \frac{1}{2}\text{trace}\left(\sigma^M\right) \tag{2.26}$$

Ils ont ensuite utilisé les équations de la thermodynamique à l'équilibre – égalité des potentiels chimiques- pour prédire le déplacement (shift) de la température produit par cisaillement dans le PS/DOP. Cette approche pseudo-thermodynamique donne de bon résultats en accord avec les observations. Néanmoins, cette théorie a été critiquée par Helfand et Fredrickson (1989) et par Onuki (1989) qui lui reprochent de minimiser l'énergie libre alors que le système sous cisaillement est hors de l'équilibre thermodynamique. De plus, cette théorie ne peut pas prédire ni décrire la structure de la solution en écoulement. Une meilleure approche pour étudier les propriétés physiques dans le régime permanent consisterait à chercher et à examiner les états stationnaires d'un

modèle dynamique. Helfand et Fredrickson (1989), ont utilisé le modèle deux fluides (two-fluid model), décrit dans l'introduction 2.1., et ont développé une description dynamique qui tient compte de l'anisotropie de la structure interne. Le tenseur taux de déformation est choisi comme variable d'état pour décrire les effets viscoélastiques. Leur théorie est capable de reproduire quelques observations (butterfly-pattern) obtenues à partir des mesures de la diffusion de la lumière, mais elle est limitée aux faibles valeurs de taux de cisaillement et ne peut décrire toutes les structures observées comme il a été mentionné par Ji (1997).

Beris et Edwards (1994), Doi (1990, 1992), Ji (1995), Lhuillier (1985, 2000), Onuki (1989, 1997), Milner (1993), van Egmond (1997) et d'autres ont introduit une variable d'élasticité qui représente le degré d'anisotropie interne. Le mélange binaire incompressible est alors caractérisé par trois variables d'état : la fraction volumique du polymère ϕ, la vitesse de l'écoulement **v**, et un tenseur symétrique du second ordre pour décrire l'anisotropie interne. Ils ont alors écrits des équations phénoménologiques en utilisant la méthode de Langevin. Pour introduire les effets de l'élasticité dans l'équation de la diffusion, Onuki (1989) utilise la compatibilité avec la thermodynamique et le gradient du potentiel chimique qui devient la force active pour la diffusion. Le potentiel chimique dépend de l'élasticité du polymère et l'équation de la concentration est couplée avec l'équation de l'écoulement. Cependant, il a négligé dans l'équation de la diffusion les effets de l'anisotropie produits par les contraintes internes. Beris et Edwards (1994), Doi (1990, 1992), Ji (1995), Lhuillier (1985, 2000), Milner (1991), Onuki (1997), van Egmond (1997), et d'autres, en utilisant deux fluides pour décrire le mélange binaire, arrivent à une formulation où le couplage entre la diffusion et les contraintes interne devient apparent et permet, par conséquent, de tenir compte de l'anisotropie observée dans le transfert de masse (migration à travers les lignes de courant, etc.).

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Chapitre 3 Objectif et liens entre les articles

Le travail de cette thèse est consacré aux comportements non standards de la diffusion observés dans les mélanges binaires et ternaires soumis ou non à un écoulement externe. Dans le chapitre 2, nous avons montré que plusieurs questions restent encore en suspens malgré la quantité de formulations consacrées à ce sujet. L'objectif de cette thèse est de contribuer à leur compréhension et à combler certaines de ces lacunes. Dans cette perspective, la procédure que nous avons adoptée et poursuivie tout au long de ce travail consiste en deux étapes

1. Choisir des observations expérimentales particulières qui restent encore mal décrites ou dont l'étude est encore non entreprise.
2. Développer ensuite des modèles théoriques en vue de les expliquer.

Cette modélisation en deux étapes s'est avérée très utile comme il sera démontré dans le corps du travail, car elle requiert, tout d'abord, de bien définir et comprendre le phénomène physique lié aux comportements observés, et ensuite, de développer une théorie dynamique adéquate pour l'expliquer. Récemment, cette dernière étape est devenue facilement réalisable à l'aide du formalisme GENERIC qui permet de déterminer les équations gouvernant l'évolution temporelle du système considéré, et de garantir que leurs solutions soient compatibles avec la thermodynamique . On procède dans une première étape à trouver leurs solutions asymptotiques (qui coincideraient avec les lois ou les modèles développés pour décrire certains cas particuliers, e.g. la loi de Fick pour les systèmes binaires, la loi de Fick généralisée pour les systèmes ternaires, etc). La deuxième étape consiste à chercher les solutions numériques et à les comparer directement avec les mesures expérimentales. Cette dernière étape se révèle décisive et indispensable pour tester et compléter les modèles développés.

Les mélanges binaires et ternaires, soumis à un écoulement imposé, sont étudiés respectivement dans les premier et quatrième articles. Dans ces mélanges, chaque composant est décrit par ses propres variables d'états. Dans les mélanges binaires (article 1), les modèles dévelopés montrent clairement et explicitement l'importance des couplages qui surviennent entre la diffusion, l'écoulement et la déformation de la structure interne. Les systèmes ternaires (article 4), révèlent, en plus des couplages ci-dessus observés dans les mélanges binaires, l'existence de nouveaux couplages qui apparaissent entre les flux de diffusion et qui génèrent des effets d'entraînement.

Pour étudier les comportements non-Fickiens, en l'absence d'un écoulement externe, et qui sont observés durant la diffusion d'un solvant (articles 2 et 3) ou de deux solvants (article 5) à travers un polymère, nous avons utilisé les modèles développés respectivement dans les articles 1 et 4 , mais en imposant les contraintes de l'équilibre mécanique et de l'incompressibilité globale. Le travail de l'article 2 et de son extension directe donnée par l'article 5 mettent en évidence l'importance du couplage entre la diffusion et la microstructure. Dans ces deux articles, la partie numérique et la comparaison avec les observations expérimentales sont consacrées aux modèles décrivant la diffusion non-Fickienne produite par l'inertie des flux de masse. Le développement entrepris dans article 3 généralise celui de l'article 2 où une étude analytique et numérique détaillée, appuyée par une comparaison directe avec l'expérience, montre l'interdépendance entre le transfert de masse et la déformation de la structure interne.

Chapitre 4.

Rheology and Diffusion in Simple and Complex Fluids

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4.1. Abstract

Diffusion and rheology in a mixture of two simple or one simple and one complex fluids are studied systematically in the framework of GENERIC modeling. The main result is a set of intrinsically consistent equations governing the time evolution of the overall mass density, overall momentum density (this equation involves explicit formulae for the scalar hydrodynamic pressure and the extra stress tensor), relative concentration of one fluid, diffusion flux, and the microstructure of the complex fluid. In the process of solving these equations we recover well known results concerning the influence of stresses on diffusion and obtain new results concerning the influence of diffusion on stresses.

4.2. Introduction

Coupling between diffusion and macroscopic overall flow is seen for example in the behavior of polymer solutions. As a specific illustration, we can mention a uniform polymer solution sheared between two parallel rotating discs. As noted by Schreiber et al. [1], the polymer in this situation tends to reduce its elastic energy and diffuses thus toward the center of the discs (see also [2]). The diffusion is, in general, non-Fickean. In this illustration the inhomogeneous flow induces diffusion. We can think also about another situation [3,4] in which a polymer solution at rest starts to flow if put into the contact with the solvent. In this illustration the diffusion (again in general non-Fickean) induces the macroscopic overall flow.

Our objective in this paper is to formulate a setting that is suitable for discussing the rheology-diffusion coupling. We shall follow the Hamiltonian modeling [5-7], in particular then its latest formulation, called GENERIC (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling) [8,9]. We begin therefore by recalling the basic physics behind this formalism. Following the spirit of the Hamiltonian modeling, we focus our attention first on the consequences of the governing equations that we want to formulate. We want to guarantee that solutions to these governing equations agree with results of certain fundamental observations. We therefore proceed as follows. First, we identify the observations that we consider to be fundamental, second, we identify the structure of the equations that guarantees that their solutions agree with results of these observations, and finally, we express the physics of the particular problem under consideration in the realization of the structure. In this paper, we choose the fundamental observations to be those constituting the experimental basis of equilibrium thermodynamics (i.e. the observations that a system left sufficiently long time without external influences reaches a state at which its behavior is well described by equilibrium thermodynamics). The mathematical structure of the equations that guarantees agreement with these observations has appeared gradually [5-8]. Roughly speaking, the vector field generating the time

evolution is a gradient of two potentials, i.e. a covector, transformed into a vector by a Poisson and a Riemannian-like structures in the space of the chosen state variables. The potentials are related to thermodynamics (they have the physical meaning of energy and entropy) and the two structures in the state space express the kinematics of the chosen state variables. The governing equations are then introduced as particular realizations of the general structure. It is in the realization where we express the particularity of the macroscopic system under consideration. The realization consists of four steps : selection of the state variables, identification of their Poisson kinematics, identification of their Riemannian-like kinematics, and finally, specification of the potentials. In this paper, we shall follow these four steps. All their necessary physical and mathematical aspects will be explained.

The rheology-diffusion coupling has been discussed previously by using various approaches [2,4,11-25]. The most important new feature of the present paper is completeness and unification. For example, we recover as particular cases some of the well known non standard diffusion equations [2-4, 11-25] that couple diffusion with stresses. With every such equation we obtain however also the corresponding expression for the extra stress tensor that couples the flow to diffusion. This result, arising naturally in the Hamiltonian modeling, is entirely new.

4.3. State Variables

The physical system that we shall discuss in this paper is a two-component fluid. One component is a solvent (a simple fluid) and the second component is a complex fluid (e.g. a polymeric fluid). The two components are assumed to form a completely miscible solution, i.e. there is no macroscopic interface inside the fluid. Both fluids are supposed to be kept at a constant and uniform temperature. In order to study the time evolution of this system, we have to choose first the quantities, called state variables, with which we shall

characterize states. We recall now the considerations involved in choosing the state variables.

First, we have to clearly specify our interests, i.e. what do we want to predict and what type of experimental observations do we want to compare with. In this paper, our interests are those of a rheologist. This means that we look at the fluid via the experimental methods developed in classical hydrodynamics and rheology. As a consequence, the basic state variables will be selected to be the classical hydrodynamics fields (i.e. fields of mass density, momentum and energy) and if this is found to be insufficient, we adopt some other fields. We want to remain however with the smallest possible number of additional fields.

How can we see whether a given set of state variables is sufficient ? To answer this question we can follow either a theoretical or an experimental approach. In the theoretical analysis, we have to begin on a more microscopic level of description (e.g. we follow all molecules composing the fluid) and to show that the time evolution of the chosen state variables is clearly separated from the time evolution of the remaining details. In the experimental analysis we have to check that the predictions based on the time evolution of the chosen state variables are reproducible in measurements. In practice neither the theoretical nor the experimental analysis can be followed completely. The choice of state variables becomes thus a guessing enterprise based on the collected experience and the trial-and-error method.

If the two components are simple fluids then we choose as state variables

$$x^{(1)} := \left(\rho_1,\ \mathbf{u}_1,\ \rho_2,\ \mathbf{u}_2\right), \tag{4.1}$$

where the symbol x denotes the set of state variables, ρ_i and $\mathbf{u}_i$ are the mass density and momentum respectively, i=1, 2 is the index referring to the component. Both ρ_i and $\mathbf{u}_i$ depend on the position vector and the time t. The upper index (4.1) in $x^{(1)}$ refers to the

first choice of state variables. Following the classical studies of diffusion [18], it is convenient to transform $x^{(1)}$ into another set of state variables, denoted $y^{(1)}$

$$y^{(1)} := (\rho, c, \mathbf{u}, \mathbf{w}) \tag{4.2}$$

by the one-to-one transformation

$$\begin{aligned} \rho &= \rho_1 + \rho_2 \\ c &= \frac{\rho_1}{\rho_1 + \rho_2} \\ \mathbf{u} &= \mathbf{u}_1 + \mathbf{u}_2 \\ \mathbf{w} &= \frac{\rho_2}{\rho_1 + \rho_2}\mathbf{u}_1 - \frac{\rho_1}{\rho_1 + \rho_2}\mathbf{u}_2 \end{aligned} \tag{4.3}$$

ρ is the total mass density, c is the concentration of the component 1, $\mathbf{u}$ is the total momentum and $\mathbf{w}$ is the relative momentum. Instead of the momentum field $\mathbf{u}$ we can also use the velocity field $\mathbf{v}$. This field will be introduced later as a field conjugate to $\mathbf{u}$ (i.e. as the derivative of the thermodynamic potential with respect to $\mathbf{u}$).

If the second component is a complex fluid then we choose

$$x^{(2)} := (\rho_1, \mathbf{u}_1, \rho_2, \mathbf{u}_2, \psi) \tag{4.4}$$

The symbols ρ_i and $\mathbf{u}_i$ have the same meaning as in (4.1), $\psi(\mathbf{r}, \mathbf{R}, t)$ is a configuration space distribution function of macromolecules (composing the second component) with the end-to-end vector $\mathbf{R}$. With this distribution function we choose to characterize the internal structure of the complex fluid. We recall that the solvent mass density ρ_1 can also be written as

$$\rho_1 = \gamma_1 \phi_1 \tag{4.5}$$

where γ_1 is the solvent material density and ϕ_1 is the volume fraction of the polymer. We shall assume that γ_1 is a constant (the assumption of material incompressibility) so that ρ_1 and ϕ_1 differ only by a constant multiplication factor of the mass density dimension (ϕ_1 is dimensionless). Without the assumption of material incompressibility we would have to adopt ϕ_1 as additional state variable.

If the transformation (4.3) is applied to $x^{(2)}$, we arrive at :

$$y^{(2)} := (\rho, c, \mathbf{u}, \mathbf{w}, \psi) \tag{4.6}$$

Alternatively, we can characterize the internal structure of the second component by a conformation tensor $\mathbf{m}$, i.e. we introduce

$$x^{(3)} := (\rho_1, \mathbf{u}_1, \rho_2, \mathbf{u}_2, \mathbf{m}) \tag{4.7}$$

The conformation tensor $\mathbf{m}$ is related to the distribution function ψ by

$$m_{\alpha\beta}(\mathbf{r}, t) = \int d\mathbf{R}\, R_\alpha R_\beta\, \psi(\mathbf{r}, \mathbf{R}, t), \qquad \alpha, \beta = 1, 2, 3 \tag{4.8}$$

By using the transformation (4.3) we also introduce

$$y^{(3)} := (\rho, c, \mathbf{u}, \mathbf{w}, \mathbf{m}) \tag{4.9}$$

4.4. Poisson Kinematics

Having chosen the state variables, our next task is to determine their kinematics. This is the first step on the way to establish the time evolution equations. First, we recall the

kinematics of $(\rho, \mathbf{u})$, i.e. the kinematics of the mass density and momentum of a one component fluid. The motion of a fluid in classical continuum mechanics is regarded as a group (Lie group) of transformation $\mathbb{R}^3 \rightarrow \mathbb{R}^3$, an element of the dual of the Lie algebra associated with this Lie group is the momentum $\mathbf{u}$. The Lie group structure induces in the dual of the Lie algebra a Poisson structure specified by the Poisson bracket [19]

$$\{A, B\} = \int d\mathbf{r} \left(u_\gamma \left[\partial_\alpha \left(A_{u_\gamma} \right) B_{u_\alpha} - \partial_\alpha \left(B_{u_\gamma} \right) A_{u_\alpha} \right] \right) \tag{4.10}$$

In (4.10) we use the following notation : A, B are sufficiently regular real valued functions of $\mathbf{u}(\mathbf{r})$, $\partial_\alpha := \partial / \partial r_\alpha$ and $A_{u_\gamma} := \delta A / \delta u_\gamma(\mathbf{r})$ is the Volterra functional derivative, the summation convention over repeated indices is used throughout this paper.

To elucidate the physical meaning of (4.10) we shall recall an alternative derivation [5,6]. Let us begin at the microscopic level, i.e. we characterize the fluid under consideration by the N-particle distribution function $f_N(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N)$, where $N \sim 10^{23}$ is the number of particles composing the fluid $(\mathbf{r}_i, \mathbf{v}_i)$, $i = 1, \ldots, N$ are the position and velocity vectors of the i^{th} particle. The kinematics of $(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N)$ is characterized by the classical canonical Poisson bracket

$$\{a, b\}^{(cm)} = \sum_{i=1}^{i=N} \left(a_{r_{i\alpha}} b_{v_{i\alpha}} - a_{v_{i\alpha}} b_{r_{i\alpha}} \right) \tag{4.11}$$

where a, b are sufficiently regular real valued functions of $(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N)$, $a_{r_{i\alpha}} = \partial a / \partial r_{i\alpha}$ The Poisson bracket specifying the kinematics of $f_N(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N)$ can be obtained by regarding f_N as elements of the dual to the Lie

algebra corresponding to the Lie group of canonical transformations in $(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N)$ [17]. In this way we arrive at

$$\{A, B\} = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \, f_N \left\{A_{f_N}, B_{f_N}\right\}^{(cm)} \tag{4.12}$$

This bracket has a clear physical interpretation : if we consider A and B to be linear functionals of f_N, i.e. we take

$$A(f_N) = \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \int d\mathbf{v}_1 \ldots d\mathbf{v}_N \, a(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N) f_N(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N) \tag{4.13}$$

and similarly

$$B(f_N) = \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \int d\mathbf{v}_1 \ldots d\mathbf{v}_N \, b(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N) f_N(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N) \tag{4.14}$$

and f_N to be the Klimonotovich distribution function

$$f_N \propto \delta(\mathbf{r}_1 - \hat{\mathbf{r}}_1)\delta(\mathbf{v}_1 - \hat{\mathbf{v}}_1) \ldots \delta(\mathbf{r}_N - \hat{\mathbf{r}}_N)\delta(\mathbf{v}_N - \hat{\mathbf{v}}_N) \tag{4.15}$$

where $\hat{\mathbf{r}}_i$ and $\hat{\mathbf{v}}_i$ are coordinates and velocities of the particles, then (4.12) clearly reduces to (4.11).

We see thus that (4.12) is a natural extension of (4.11) to the description that uses distribution functions rather than discrete position coordinates and velocities of the particles. From (4.12) we now arrive at (4.10) by simply expressing $\mathbf{u}(\mathbf{r})$ in terms of f_N :

$$\mathbf{u}(\mathbf{r}) = \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N \int d\mathbf{v}_1 \ldots \int d\mathbf{v}_N \, f_N\left(\sum_{i=1}^{i=N} m\mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i)\right) \tag{4.16}$$

where m is the mass of one particle. If we restrict (4.12) to functionals A, B that depend on f_N only through their dependence on $u(r)$ (see (4.16)), we arrive at (4.10) by replacing

$$A_{f_N(r_1,v_1,\ldots r_N,v_N)} \text{ in (4.12) by } \int dr\, A_{u_\alpha(r)} \frac{\delta u_\alpha(r)}{\delta f_N(r_1, v_1,\ldots,r_N, v_N)} .$$

If in addition to $u(r)$ the fluid is also characterized by the mass density $\rho(r)$ then (4.10) extends to

$$\begin{aligned} \{A, B\} = \int dr \Big(& \rho \left[\partial_\alpha \left(A_\rho \right) B_{u_\alpha} - \partial_\alpha \left(B_\rho \right) A_{u_\alpha} \right] \\ & + u_\gamma \left[\partial_\alpha \left(A_{u_\gamma} \right) B_{u_\alpha} - \partial_\alpha \left(B_{u_\gamma} \right) A_{u_\alpha} \right] \Big) \end{aligned} \tag{4.17}$$

The new term expresses that $\rho(r)$ is advected by the flow generated by $u(r)$ [19]. This Poisson bracket can also be simply derived from (4.12). In addition to $u(r)$ given by (4.16) we also introduce

$$\rho(r) = \int dr_1 \ldots \int dr_N \int dv_1 \ldots \int dv_N \; f_N \left(\sum_{i=1}^{i=N} m \delta (r - r_i) \right) \tag{4.18}$$

Then , we restrict (4.12) to functionals A, B that depend on f_N only through their dependence on $\rho(r)$ and $u(r)$ (see (4.18) and (4.16)). The Volterra functional derivative in (4.12) is now replaced by

$$\begin{aligned} A_{f_N(r_1, v_1,\ldots r_N, v_N)} = \int dr \Bigg(& A_{\rho(r)} \frac{\delta \rho(r)}{\delta f_N(r_1, v_1,\ldots,r_N, v_N)} \\ & + A_{u_\alpha(r)} \frac{\delta u_\alpha(r)}{\delta f_N(r_1, v_1,\ldots,r_N, v_N)} \Bigg) \end{aligned} \tag{4.19}$$

Straightforward calculations lead directly from (4.12) to (4.17).

We now proceed to specify the Poisson kinematics of $x^{(1)}$ and $y^{(1)}$ (see (4.1), (4.7)). As for $x^{(1)}$, the Poisson kinematics is simply the sum of (4.17) for component 1 and (4.17)

for component 2. The one-to-one transformation (4.3) transforms this Poisson bracket into another Poisson bracket

$$
\begin{aligned}
\{A, B\} = \int dr \Big(& \rho \left[\partial_\alpha\left(A_\rho\right)B_{u_\alpha} - \partial_\alpha\left(B_\rho\right)A_{u_\alpha}\right] \\
& + u_\gamma \left[\partial_\alpha\left(A_{u_\gamma}\right)B_{u_\alpha} - \partial_\alpha\left(B_{u_\gamma}\right)A_{u_\alpha}\right] \\
& - \partial_\alpha(c) \left[A_c B_{u_\alpha} - A_{u_\alpha} B_c\right] \\
& + w_\gamma \left[\partial_\alpha\left(A_{w_\gamma}\right)B_{u_\alpha} - \partial_\alpha\left(B_{w_\gamma}\right)A_{u_\alpha}\right] \\
& + w_\gamma \left[\partial_\alpha\left(A_{u_\gamma}\right)B_{w_\alpha} - \partial_\alpha\left(B_{u_\gamma}\right)A_{w_\alpha}\right] \\
& - w_\gamma \left[\partial_\alpha\left(c\, A_{w_\gamma}\right)B_{w_\alpha} - \partial_\alpha\left(c\, B_{w_\gamma}\right)A_{w_\alpha}\right] \\
& + (1-c)(cu_\gamma + w_\gamma) \left[\partial_\alpha\left(A_{w_\gamma}\right)B_{w_\alpha} - \partial_\alpha\left(B_{w_\gamma}\right)A_{w_\alpha}\right] \\
& + \rho\, c\,(1-c) \left[\partial_\alpha\left(\frac{1}{\rho}A_c\right)B_{w_\alpha} - \partial_\alpha\left(\frac{1}{\rho}B_c\right)A_{w_\alpha}\right] \\
& - \rho\, c\,(1-c) \left[\partial_\alpha\left(\frac{u_\gamma}{\rho}A_{w_\gamma}\right)B_{w_\alpha} - \partial_\alpha\left(\frac{u_\gamma}{\rho}B_{w_\gamma}\right)A_{w_\alpha}\right]\Big)
\end{aligned}
\tag{4.20}
$$

expressing the Poisson kinematics of $y^{(1)}$. The calculations leading from the bracket for $x^{(1)}$ (the sum of two brackets (4.17), one for (ρ_1, u_1) and the other for (ρ_2, u_2)) to the bracket (4.20) for $y^{(1)}$ consists of expressing, by using (4.3), A_{ρ_1}, A_{ρ_2}, A_{u_1}, A_{u_2}, B_{ρ_1}, B_{ρ_2}, B_{u_1}, B_{u_2} in terms of A_ρ, A_c, A_u, A_w, B_ρ, B_c, B_u, B_w.

Next, we turn our attention to the Poisson kinematics of the state variables $x^{(2)}$ and $y^{(2)}$ (see (4.4), (4.6)). We recall [5-9] that the Poisson bracket specifying the Poisson kinematics of a one-component complex fluid whose states are characterized by (ρ, u, ψ) is

$$\{A, B\} = \int dr \Big(\rho \left[\partial_\alpha\left(A_\rho\right)B_{u_\alpha} - \partial_\alpha\left(B_\rho\right)A_{u_\alpha}\right] + u_\gamma\left[\partial_\alpha\left(A_{u_\gamma}\right)B_{u_\alpha} - \partial_\alpha\left(B_{u_\gamma}\right)A_{u_\alpha}\right] + \int dr \int dR\, \psi\left[\partial_\gamma\left(A_\psi\right)B_{u_\gamma} - \partial_\gamma\left(B_\psi\right)A_{u_\gamma}\right] + \int dr \int dR\, \psi R_\beta \left(\frac{\partial}{\partial R_\gamma}\left(A_\psi\right)\partial_\beta\left(B_{u_\gamma}\right) - \frac{\partial}{\partial R_\gamma}\left(B_\psi\right)\partial_\beta\left(A_{u_\gamma}\right)\right) \tag{4.21}$$

The two terms that involve ψ express the advection by the flow generated by **u**. The Poisson bracket expressing the kinematics of y [(2)] is :

$$\{A, B\}^{(2)} = \{A, B\}^{(1)} + \int dr \int dR \quad \psi\left[\partial_\gamma\left(A_\psi\right)B_{u_\gamma} - \partial_\gamma\left(B_\psi\right)A_{u_\gamma}\right] + \psi R_\beta\left[\frac{\partial}{\partial R_\gamma}\left(A_\psi\right)\partial_\beta\left(B_{u_\gamma}\right) - \frac{\partial}{\partial R_\gamma}\left(B_\psi\right)\partial_\beta\left(A_{u_\gamma}\right)\right] - \psi c\left[\partial_\gamma\left(A_\psi\right)B_{w_\gamma} - \partial_\gamma\left(B_\psi\right)A_{w_\gamma}\right] - \psi R_\beta\left[\frac{\partial}{\partial R_\gamma}\left(A_\psi\right)\partial_\beta\left(cB_{w_\gamma}\right) - \frac{\partial}{\partial R_\gamma}\left(B_\psi\right)\partial_\beta\left(cA_{w_\gamma}\right)\right]\Big) \tag{4.22}$$

Finally, we determine the Poisson kinematics of x [(3)] and y [(3)] (see (4.7) and (4.9)). We first consider again only a one component complex fluid. The kinematics of (ρ, **u**, **m**) expressing the simple advection of the conformation tensor **m** is expressed in the Poisson bracket [5-9]

$$\{A,B\} = \int dr \Big(\rho\left[\partial_\alpha\left(A_\rho\right)B_{u_\alpha} - \partial_\alpha\left(B_\rho\right)A_{u_\alpha}\right] + u_\gamma\left[\partial_\alpha\left(A_{u_\gamma}\right)B_{u_\alpha} - \partial_\alpha\left(B_{u_\gamma}\right)A_{u_\alpha}\right] + m_{\gamma\beta}\left[\partial_\alpha\left(A_{m_{\gamma\beta}}\right)B_{u_\alpha} - \partial_\alpha\left(B_{m_{\gamma\beta}}\right)A_{u_\alpha}\right] + m_{\alpha\beta}\left[A_{m_{\gamma\beta}}\partial_\alpha\left(B_{u_\gamma}\right) - B_{m_{\gamma\beta}}\partial_\alpha\left(A_{u_\gamma}\right)\right] + m_{\alpha\beta}\left[A_{m_{\beta\gamma}}\partial_\alpha\left(B_{u_\gamma}\right) - B_{m_{\beta\gamma}}\partial_\alpha\left(A_{u_\gamma}\right)\right]\Big) \tag{4.23}$$

The last three lines are the terms expressing the simple advection of $\mathbf{m}$. They are obtained simply from the second term on the right hand side of (4.21) (i.e. the term expressing the simple advection of ψ) by using the relation (4.8) between ψ and $\mathbf{m}$. The Poisson bracket expressing the kinematics of $y^{(3)}$ (see (4.9)) is thus

$$
\begin{aligned}
\{A,B\}^{(3)} = \{A,B\}^{(3)} & \\
+ \int d\mathbf{r} \quad & m_{\gamma\beta}\left[\partial_\alpha\left(A_{m_{\gamma\beta}}\right)B_{s_\alpha} - \partial_\alpha\left(B_{m_{\gamma\beta}}\right)A_{s_\alpha}\right] \\
& + m_{\alpha\beta}\left[A_{m_{\gamma\beta}}\partial_\alpha\left(B_{s_\gamma}\right) - B_{m_{\gamma\beta}}\partial_\alpha\left(A_{s_\gamma}\right)\right] \\
& + m_{\alpha\beta}\left[A_{m_{\alpha\gamma}}\partial_\beta\left(B_{s_\gamma}\right) - B_{m_{\alpha\gamma}}\partial_\beta\left(A_{s_\gamma}\right)\right] \\
& - c\,m_{\gamma\beta}\left[\partial_\alpha\left(A_{m_{\gamma\beta}}\right)B_{w_\alpha} - \partial_\alpha\left(B_{m_{\gamma\beta}}\right)A_{w_\alpha}\right] \\
& - m_{\alpha\beta}\left[A_{m_{\gamma\beta}}\partial_\alpha\left(c\,B_{w_\gamma}\right) - B_{m_{\gamma\beta}}\partial_\alpha\left(c\,A_{w_\gamma}\right)\right] \\
& - m_{\alpha\beta}\left[A_{m_{\alpha\gamma}}\partial_\beta\left(c\,B_{w_\gamma}\right) - B_{m_{\alpha\gamma}}\partial_\beta\left(c\,A_{w_\gamma}\right)\right]
\end{aligned}
\tag{4.24}
$$

4.5. Governing Equations

As already pointed out in the Introduction, our objective is to introduce time evolution equations whose solutions are guaranteed to agree with equilibrium thermodynamics. This means that in the absence of external forces, the fluids reach (as time $t \to \infty$) a state, called an equilibrium state, at which its behavior is found to be well described by equilibrium thermodynamics. We thus look for a structure of the time evolution equations that guarantees this property of their solutions. Such a structure has been identified in [5-9]. We shall now present it. It is important to stress that the way we present (and justify) the structure in this paper is only one among many that have been explored (see Refs. [5-9]).

Since the temperature T has been supposed to be kept constant. We present the general structure only for isothermal systems. Let x denote the state variables and Φ (x, T) the Helmholtz free energy. We say that Φ (x, T) is a Helmholtz free energy if :

i) $$\frac{d\Phi}{dt} \leq 0 \qquad (4.25)$$

ii) $\Phi\,(x_{eq}(T), T)$ is the equilibrium thermodynamic free energy expressing the fundamental relation; $x_{eq}(T)$ is a state at which Φ reaches its minimum, i.e.

$$\left(\frac{\delta\Phi}{\delta x}\right)_{x_{eq}(T)} = 0 \qquad (4.26)$$

The inequality (4.25) together with the requirement that Φ is a convex function in a neighborhood of x_{eq} allows to interpret Φ as a Lyapunov function corresponding to the approach of x to x_{eq} as $t \rightarrow \infty$. We thus conclude that $x_{eq}(T)$, called an equilibrium state, is the state approached as $t \rightarrow \infty$.

The problem now is to introduce the equation governing the time evolution of x so that (4.25) holds. This problem does not have, of course, a unique solution. In general, there are many time evolutions of x that will imply (4.25). Other considerations and requirements are needed to narrow down the solution. Based on Refs. [5-9], we suggest the following time evolution equation :

$$\frac{dA}{dt} = \{A, \Phi\} - [A, \Phi] \qquad (4.27)$$

This equation is required to hold for all real valued (sufficiently regular) functionals A(x). The following notation has been used in (4.27), Φ denotes the free energy, $\{\ ,\ \}$ is the Poisson bracket expressing kinematics of x (see Section III), and $[\ ,\ ]$ is a dissipation bracket satisfying the following properties :

$$\begin{aligned} &[A, A] \geq 0 \\ &[A, B] = [B, A] \\ &[A, B] \text{ is a bilinear function of } \delta A/\delta x,\ \delta B/\delta x \end{aligned} \qquad (4.28)$$

Equation (4.27) is only a special case of a richer structure, called *GENERIC* (General Equation for Non Equilibrium Reversible and Irreversible Coupling) introduced in [8,9] but (4.27) will be sufficient for the applications considered in this paper.

We now show that (4.27) indeed implies (4.25). By writing (4.27) with $A = \Phi$, we clearly obtain (4.25) since $\{\Phi,\Phi\}=0$ (due to the antisymmetry property of Poisson brackets) and $[\Phi,\Phi] \geq 0$ due to (4.28)). The time evolution (4.27) with the second term on the right hand side missing is called a nondissipative time evolution equation (since for this equation $\frac{d\Phi}{dt} = 0$) and also a Hamiltonian (or Poisson) equation since $\{\ ,\ \}$ is a Poisson bracket. The second term on the right hand side of (4.27) introduces the dissipation (i.e. $\frac{d\Phi}{dt} \leq 0$). This is also the reason why we call the bracket $[\ ,\ ]$ a dissipation bracket.

Next, we return to the particular problem of a two component fluids discussed in this paper. In Section 4.6 we introduce a particular realization of (4.27) corresponding to a mixture of two simple fluids while in Section 4.7 we generalize the analysis to complex fluids. By a realization of (4.27) we mean a specification of state variables x (this has already been done in Section 4.3), a specification of the Poisson bracket $\{\ ,\ \}$ (this has also already been done, see Section 4.4), a specification of the dissipation bracket $[\ ,\ ]$ to be done below, and a specification of the free energy Φ.

4.6. Diffusion with Inertia in Simple Fluids

In this section, we look for a realization of Eq. (4.27) corresponding to a binary mixture of simple fluids. We begin by selecting the state variables. This has already been discussed in Section 4.3 where we decided to choose the state variables (4.2). We have also already found their Poisson kinematics (4.20). Next, we turn to the dissipation bracket $[\ ,\ ]$ and suggest the following one :

$$[A, B] = \int dr\ \mathbf{D}_A{}^T . \eta . \mathbf{D}_B + \int dr\ \mathbf{D}_{A_v}{}^T . \eta_v . \mathbf{D}_{B_v} + \int dr\, A_{w_\alpha} \frac{\Lambda}{2} B_{w_\alpha} \tag{4.29}$$

where η, η_v are second order tensors that account respectively for the shear and bulk viscosities. We define them as follows :

$$\eta = \tfrac{1}{4}\begin{pmatrix} \eta & \nu \\ \nu & \eta^r \end{pmatrix} \tag{4.30}$$

$$\eta_v = \tfrac{1}{2}\begin{pmatrix} \eta_v & \nu_v \\ \nu_v & \eta_v{}^r \end{pmatrix} \tag{4.31}$$

η, η^r, ν, η_v, η^r_v, ν_v are viscosity coefficients whose physical content will be specified later, $\mathbf{D}_X$ and $\mathbf{D}_{X_v}$ (where X = A, B) are gradients of the total and the relative momenta given by

$$\mathbf{D}_X{}^T = \left(\partial_\alpha X_{u_\beta} + \partial_\beta X_{u_\alpha},\ \partial_\alpha X_{w_\beta} + \partial_\beta X_{w_\alpha}\right) \tag{4.32}$$

$$\mathbf{D}_{X_v}{}^T = \left(\partial_\alpha X_{u_\alpha},\ \partial_\alpha X_{w_\alpha}\right) \tag{4.33}$$

The dissipation bracket (4.29) written explicitly becomes

$$\begin{aligned}
[A,B] = {} & \int dr \left(\partial_\alpha A_{u_\beta} + \partial_\beta A_{u_\alpha}\right)\frac{\eta}{4}\left(\partial_\alpha B_{u_\beta} + \partial_\beta B_{u_\alpha}\right) + \left(\partial_\alpha A_{u_\alpha}\right)\frac{\eta_v}{2}\left(\partial_\alpha B_{u_\alpha}\right) \\
& + \int dr \left(\partial_\alpha A_{w_\beta} + \partial_\beta A_{w_\alpha}\right)\frac{\eta^r}{4}\left(\partial_\alpha B_{w_\beta} + \partial_\beta B_{w_\alpha}\right) + \left(\partial_\alpha A_{w_\alpha}\right)\frac{\eta^r_v}{2}\left(\partial_\alpha B_{w_\alpha}\right) \\
& + \int dr \left(\partial_\alpha A_{u_\beta} + \partial_\beta A_{u_\alpha}\right)\frac{\nu}{2}\left(\partial_\alpha B_{w_\beta} + \partial_\beta B_{w_\alpha}\right) + \left(\partial_\alpha B_{u_\alpha}\right)\nu_v\left(\partial_\alpha B_{w_\alpha}\right) \\
& + \int dr\ A_{w_\beta}\frac{\Lambda}{2} B_{w_\beta}
\end{aligned} \tag{4.34}$$

wherein Λ is a phenomenological coefficient whose physical meaning will be established later on.

We easily verify that (4.29) satisfies the properties (4.28) provided that η, η_v ,are positive definite matrices i.e.

$$\begin{cases} \eta > 0 \\ \eta^r > 0 \\ \nu < \sqrt{\eta\eta^r} \end{cases} \qquad \text{and} \qquad \begin{cases} \eta_v > 0 \\ \eta_v^r > 0 \\ \nu_v < \sqrt{\eta_v\eta_v^r} \end{cases}$$

and Λ a positive parameter. It will be shown below that the first line on the right hand side of (4.34) accounts for the Navier-Stokes dissipation (η and η_v are the shear and bulk viscosity coefficients respectively). The second line on the right hand side of (4.34), that we have introduced by analogy to the first one, has an equivalent meaning and can be regarded as representing the viscous dissipation corresponding to the relative diffusive motion. Its significance will appear subsequently when formulating the evolution equations for the concentration and for the relative momentum $\mathbf{w}$. We will show its close relationship to the osmotic pressure and thus we shall provide a clarification of the relationship between hydrodynamic and osmotic pressures. The coefficients (η^r, η_v^r) are respectively the relative shear and the relative bulk viscosities. They express the resistance encountered by diffusing penetrants when moving from one fluid into the other. The third line on the right hand side of (4.34) can be interpreted as a dissipation resulting from the coupling between total and relative motions. Finally, the last term expresses a direct dissipation of $\mathbf{w}(\mathbf{r})$. We shall see below that the phenomenological coefficient Λ is related to the diffusion coefficient.

What remains is to specify the free energy Φ. We shall postpone this task and write first Eq. (4.27) in a more explicit form but with Φ left undetermined. The easiest way to

obtain from (4.27) the time evolution equations for (ρ, u, c, w) is the following : the left hand side of (4.27) can be given as

$$\frac{dA}{dt} = \int dr \left(A_\rho \frac{\partial \rho}{\partial t} + A_{u_\alpha} \frac{\partial u_\alpha}{\partial t} + A_c \frac{\partial c}{\partial t} + A_{w_\alpha} \frac{\partial w_\alpha}{\partial t} \right) \qquad (4.35)$$

The right hand side of (4.27) can also be recast, by using integration by parts and boundary conditions for which all the integrals over the limits of the domain of integration are equal zero, into the form

$$\{A, \Phi\} - [A, \Phi] = \int dr (A_\rho \textcircled{1} + A_{u_\alpha} \textcircled{2}_\alpha + A_c \textcircled{3} + A_{w_\alpha} \textcircled{4}_\alpha) \qquad (4.36)$$

where $\textcircled{1}, \ldots, \textcircled{4}$ represent the terms arising in the calculations. From equations (4.35) and (4.36) and by requiring that the equality holds for all functions A, we obtain the time evolution equations

$$\frac{\partial \rho}{\partial t} = \textcircled{1}, \qquad \frac{\partial u_\alpha}{\partial t} = \textcircled{2}_\alpha,$$

$$\frac{\partial c}{\partial t} = \textcircled{3} \qquad \text{and} \qquad \frac{\partial w_\alpha}{\partial t} = \textcircled{4}_\alpha \qquad (4.37)$$

or in explicit form

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha (\rho \Phi_{u_\alpha}) \qquad (4.38)$$

$$\frac{\partial u_\alpha}{\partial t} = -\partial_\gamma\left(u_\alpha \Phi_{u_\gamma}\right) - \partial_\alpha p - \partial_\gamma \tau_{\gamma\alpha} \tag{4.39}$$

$$\frac{\partial c}{\partial t} = -\Phi_{u_\alpha}\partial_\alpha(c) - \frac{1}{\rho}\partial_\alpha\left(\rho\, c\,(1-c)\,\Phi_{w_\alpha}\right) \tag{4.40}$$

$$\begin{aligned}\frac{\partial w_\alpha}{\partial t} = & -\partial_\gamma\left(w_\alpha \Phi_{u_\gamma}\right) - w_\gamma \partial_\alpha\left(\Phi_{u_\gamma}\right) - (1-c)\partial_\alpha \pi_1 + c\partial_\alpha \pi_2 \\ & -(1-2c)\partial_\gamma\left(\tau^{d.e.}_{\gamma\alpha}\right) + \left(\tau^{d.e.}_{\alpha\gamma} + tr\left(\tau^{d.e}\right)\delta_{\alpha\gamma}\right)\partial_\gamma c \\ & -\rho\, c\,(1-c)\left(\left(\partial \times \frac{u}{\rho}\right) \times \Phi_w\right)_\alpha - \partial_\gamma\left(\tau^r_{\gamma\alpha}\right) - \Lambda\, \Phi_{w_\alpha}\end{aligned} \tag{4.41}$$

The terms in Eqs. (4.38)-(4.41) that involve new, so far unexplained, symbols will be written explicitly below. Next, we shall take Eqs. (4.38)-(4.41), one after the other, write them explicitly and discuss their physical content.

Equation (4.38) is the classical local conservation law of mass. We see that Φ_u is the velocity field. Indeed, we recall that the Helmholtz free energy

$$\Phi = E - T\,S, \tag{4.42}$$

where E is the energy, S the entropy and T the constant temperature (a constant parameter in this paper). If S is independent of **u** and

$$E = E_{kin} + \tilde{E} \tag{4.43}$$

where $E_{kin} = \int dr\, \frac{u^2}{2\rho}$ is the global kinetic energy and $\tilde{E}$ is the potential energy and the part of the kinetic energy depending on **w** ($\tilde{E}$ is independent of **u**) then $\Phi_{u_\alpha} = \frac{u_\alpha}{\rho}$ is the global velocity.

Equation (4.39) is the classical local conservation law for the momentum **u**, p is the scalar hydrodynamic pressure expressed by

$$p = -\varphi + \rho\varphi_{\rho} + u_{\alpha}\varphi_{u_{\alpha}} + w_{\alpha}\varphi_{w_{\alpha}} \tag{4.44}$$

where φ is the density of Φ, i.e. $\Phi = \int dr\, \varphi(r)$, and the extra stress tensor expressed by

$$\begin{aligned}\tau_{\alpha\gamma} = \tau_{\alpha\gamma}^{d.e.} &- \eta\left(\partial_{\alpha}\Phi_{u_{\gamma}} + \partial_{\gamma}\Phi_{u_{\alpha}}\right) - \eta_{v}\left(\partial_{\beta}\Phi_{u_{\beta}}\right)\delta_{\alpha\gamma} \\ &- \nu\left(\partial_{\alpha}\Phi_{w_{\gamma}} + \partial_{\gamma}\Phi_{w_{\alpha}}\right) - \nu_{v}\left(\partial_{\beta}\Phi_{w_{\beta}}\right)\delta_{\alpha\gamma} \quad ,\end{aligned} \tag{4.45}$$

$$\tau_{\alpha\gamma}^{d.e.} = w_{\alpha}\Phi_{w_{\gamma}} \tag{4.46}$$

Using the terminology introduced in classical hydrodynamics, expressions (4.44)-(4.46) represent constitutive relations. We emphasize that these constitutive relations arise in the calculations involved in (4.37). In our analysis they thus arise as a consequence of the Poisson kinematics and of the choice (4.34) of the dissipation bracket. This is in sharp contrast to the classical approach where the arguments leading to the constitutive relations are separate from the arguments on which the time evolution equations are based. Now we interpret physically the constitutive relations (4.44)-(4.46). We note first that (44) represents a generalization of the local equilibrium expression for the pressure. Indeed, if the field **w** is absent then (4.44) reduces to the result known from classical hydrodynamics [5-9] (i.e. p is related pointwise to ρ and T as in equilibrium provided **u** = 0). We emphasize that we did not assume the fluid as a whole to be incompressible (i.e. ρ is a state variable, it can change in **r** as well as in t). If on the other hand, we would assume the incompressibility then ρ would not serve as a state variable, the second term on the right hand side of (4.44) would be thus missing and, most importantly, the requirement that ρ does not change neither in space nor in time implies constraint $\partial_{\gamma}\Phi_{u_{\gamma}} = 0$ which drives the fluid out of the generalized local equilibrium. In such a case the local hydrodynamic

pressure would be determined by $\partial_\gamma \Phi_{u_\gamma} = 0$ together with (4.39) and not by (4.44).The contribution $\tau^{d.e.}_{\alpha\gamma}$ to the extra stress tensor $\tau_{\alpha\gamma}$ is the nondissipative (i.e. elastic and time reversible) part of the stress. It appears as a consequence of the Poisson kinematics. The term $\tau^{d.e}$ is mentioned in [16] but it is absent, to the best of our knowledge , in all the models of the rheology-diffusion coupling. Since $\tau^{d.e.}$ is quadratic and higher order in **w**, its contribution to the stress is, in most situations, small. The second and the third terms on the right hand side of (4.45) arise due to the presence of the dissipation bracket. These terms represent dissipation stresses of the standard Navier-Stokes type. The coefficients η and η_v are the shear viscosity and the bulk viscosity coefficients respectively. The last two terms are new. They represent a dissipative contribution to the stress due to the presence of the gradient of the relative momentum **w**. The physical content of this term will become clearer in the next section.

Equation (4.40) is a classical diffusion equation (also called first Fick's law). The diffusion flux **J** is given by

$$J_\alpha = \rho c(1-c)\Phi_{w_\alpha} \tag{4.47}$$

Equation (4.41) is the constitutive relation for the diffusion flux. We shall see later that it indeed reduces in a particular situation to the second Fick law. In its complete version, Eq. (4.41) is a time evolution equation for **w**. We shall compare it to Eq. (4.39). Of course, there is an essential difference between (4.39) and (4.41). Equation (4.39) is a local conservation law (i.e. the right hand side is a divergence of a tensor so that the total momentum $\int d\mathbf{r}\, \mathbf{u}(\mathbf{r})$ is conserved) while $\int d\mathbf{r}\, \mathbf{w}(\mathbf{r})$ is not conserved. We can however recognize in (4.39) and (4.41) terms having the same physical meaning. The first term on the right hand side of (41) represents the simple advection. The second , third and fourth terms play the role of - $\partial_\alpha p$ in (4.39). We note that the hydrodynamic pressure is now replaced by two scalar osmotic pressures

$$\pi_i = -\tilde{\varphi} + \rho_i \tilde{\varphi}_{i\,\rho_i} + w_\gamma \tilde{\varphi}_{i w_\gamma}, \qquad i=1,2 \tag{4.48}$$

where $\tilde{\varphi}_1 = \varphi|_{u,\rho_2}$, $\tilde{\varphi}_2 = \varphi|_{u,\rho_1}$, i.e. $\tilde{\varphi}_1$ is the free energy density evaluated at u and ρ_2; $\tilde{\varphi}_1$ is thus only a function of ρ_1 and w. Similarly $\tilde{\varphi}_2$ is the free energy density evaluated at u and ρ_1, i.e. $\tilde{\varphi}_2$ is a function of ρ_2 and w only. The fifth, sixth and seventh terms play a similar role as $-\partial_\gamma \tau^{d.e.}_{\alpha\gamma}$ in (39). The eighth term expresses the change of w due to the rotation caused by the vorticity. All the first eight terms on the right hand side of (4.41) are nondissipative (time reversible). They arise solely from the Poisson kinematics. They do not involve any unspecified parameters (except, of course, the free energy Φ). Only the remaining last two terms on the right hand side of (4.41) are dissipative. They arise from the dissipation bracket (4.34). The ninth term,

$$\begin{aligned} \tau^{r}_{\gamma\alpha} = &-\eta^{r}\left(\partial_\gamma \Phi_{w_\alpha} + \partial_\alpha \Phi_{w_\gamma}\right) - \eta^{r}_{v}\left(\partial_\beta \Phi_{w_\beta}\right)\delta_{\alpha\gamma} \\ &-\nu\left(\partial_\gamma \Phi_{u_\alpha} + \partial_\alpha \Phi_{u_\gamma}\right) - \nu_v\left(\partial_\beta \Phi_{u_\beta}\right)\delta_{\alpha\gamma} \end{aligned} \tag{4.49}$$

represents the dissipation stress due to the presence of the gradients of the velocities Φ_w and Φ_u (a force created to resist deformations produced by both the overall and the internal flows). The stress $\tau^{r}_{\gamma\alpha}$ involving η^{r}, η^{r}_{v}, ν and ν_v will be discussed in more detail in Section 4.7. A stress tensor of similar type has been introduced previously in [20] in the context of diffusion in polymeric fluids. Finally, the last term on the right hand side of (4.41) represents a direct relaxation of the relative velocity Φ_w. A term of this type is, of course, absent in (4.39) since it would violate the conservation of the total momentum $\int dr\, u(r)$. More about the physical content of the parameters Λ, η, η_v, η^{r}, η^{r}_{v}, ν, ν_v appearing in the dissipative part of the governing equations (4.38)-(4.41) will be revealed from the analysis of solutions in the next subsection.

Before discussing solutions of Eqs. (4.38)-(4.41) we recall that the Hamiltonian modeling has been used before [21-6] to study diffusion. In Ref [21] w is not treated as an independent state variable. The new, nonstandard, features of the diffusion in polymeric fluids have to be thus brought only in the dissipation bracket. In our study, on the other hand, the new features arise in the Poisson kinematics that is completely rigorous. We shall see in Section 4.7, in the context of polymeric fluids, that also the new stresses involving η^r and ν arise in the Poisson kinematics. In Ref [6] the field w is treated as an independent state variable but the Poisson kinematics used in Ref.[6] is an incomplete version of the kinematics derived in this paper (in Section 4.4)

4.6.1. Properties of solutions of Eqs. (4.38)-(4.41)

First, we look at solutions of Eqs. (4.38) - (41) for $t \to \infty$. We wish to connect our theoretical findings with observations that represent the experimental basis of equilibrium thermodynamics (i.e. a system that is left without an external influence reaches a state, called an equilibrium state, at which its behavior is well described by equilibrium thermodynamics). We recall that the main reason why we introduce Eq. (4.27) is to have an equation whose solutions agree with this observation [5-9]. Indeed, the free energy Φ plays in (4.27) the role of the Lyapunov function and as t tends to ∞ solutions to (4.27) approach the minimum of Φ. Since Eqs. (4.38)-(4.41) are a particular realization of Eq. (4.27), this property of solutions of (4.27) is shared with the properties of solution of Eqs. (4.38)-(4.41). It is worth to emphasize that this property of the solutions was obtained with the free energy Φ still left undetermined and the parameters Λ, η, η_v, η^r, η^r_v, ν, ν_v required to satisfy only the inequalities below Eq. (4.34).

Next, we continue to search for the $t \to \infty$ behavior of solutions but now we are not only interested at the final product of the evolution but also at the final stage of the approach to it. In other words, we look at the final stage of the approach to equilibrium. We assume that w evolves faster than the rest of the state variables. At the final stage of

the approach to equilibrium we can therefore consider $\partial w/\partial t \approx 0$ and also w itself vanishes (since $\Phi \sim w^2$ and thus at equilibrium $w = 0$). From Eq. (4.41) we thus have (all terms quadratic and higher order in w and u)

$$\Lambda \Phi_{w_\alpha} = -\rho c(1-c)\partial_\alpha\left(\frac{\Phi_c}{\rho}\right) \tag{4.50}$$

(since $-(1-c)\,\partial_\alpha \pi_1 + c\partial_\alpha \pi_2 = -\rho c(1-c)\partial_\alpha\left(\frac{\Phi_c}{\rho}\right)$)

Together with Eq. (4.47) we obtain

$$J_\alpha = -\frac{(\rho c(1-c))^2}{\Lambda}\partial_\alpha\left(\frac{\Phi_c}{\rho}\right) \tag{4.51}$$

which is the first Fick law. We thus conclude that the final stage of the approach to the equilibrium is governed by Fick diffusion. Furthermore, it follows from (4.51) that the parameter Λ, introduced originally in the dissipation bracket (4.29), is related to the diffusion coefficient of the first Fick law. Note if $\Lambda \geq 0$ (that is needed in order that (38)-(41) represents a particular realization of GENERIC) then the diffusion coefficient $(\rho c(1-c))^2/\Lambda$ is also nonnegative. On the other hand (4.51) does not imply anything about the dependence on ρ and c since Λ is at this point unspecified (except the requirement $\Lambda > 0$) function of the state variables (4.2).

The analysis of the final stage of the approach towards equilibrium governed by Eqs. (4.38)-(4.41) does not only allow us to recover the Fick diffusion but also the rheology in this stage of the evolution is revealed. Let us assume that Φ, as a function of w, behaves as

$$\Phi = 1/2\, A w^2 \tag{4.52}$$

for small w, A is a constant. Introducing (4.52) into (4.46), we obtain

$$\tau^{d.e.}_{\alpha\gamma} = \frac{(\rho c(1-c))^2}{A\Lambda^2}\partial_\alpha\left(\frac{\Phi_c}{\rho}\right)\partial_\gamma\left(\frac{\Phi_c}{\rho}\right) \tag{4.53}$$

We thus see that inhomogeneities in the concentration create additional stresses that are of the second order in the gradient of c. These stresses are elastic and therefore the mixture of simple fluids with large concentration gradients is, from the rheological point of view, a viscoelastic fluid.

If $\partial w/\partial t$ is not small then Eqs. (4.38)-(4.41) describe non standard diffusion and coupled with it rheology. The occurrence of the time derivative of w in the constitutive Eq. (4.41) signifies the presence of inertia in the diffusion. We now ask the following question : when does the nonstandard diffusion in simple fluids described by Eqs. (4.38)-(4.41) manifest itself. In most instances, the last term on the right hand side of (4.41) is dominant (i.e. the relaxation time $\sim\rho\Lambda^{-1}$ of w is very small) and then, as shown above, the diffusion is purely Fickean. In fact, the main reason to have worked out as a first example the case of simple fluids is to prepare the setting for complex fluids that are discussed in the next section. We can however identify a situation at which the nonstandard diffusion and associated with it complex rheology is clearly visible also in simple fluids. We see from Eqs. (4.38)-(4.41) that the nonstandard features of diffusion and rheology can manifest themselves in simple fluids that are strongly inhomogeneous in both the concentration and the flow. Such situations arise during mixing. We recall that we assume that all fluids considered in this paper are completely miscible. To enhance the formation of a homogeneous mixture the diffusion is often supplemented by creating complex, strongly inhomogeneous flows. It follows indeed from Eqs. (4.38)-(4.41) that the diffusion becomes then nonstandard and the fluid viscoelastic (even if the two components, considered separately, as well as the homogeneous mixture, are inelastic).

It is useful to put Eqs. (4.38)-(4.41) into the context of extended irreversible thermodynamics [22, 13, 14]. Let us consider the classical Fickean diffusion and let us try to extend it by following the spirit of extended irreversible thermodynamics. The first step is the enlargement of the set of state variables by adopting the diffusion flux as a new state variable. The requirement of the compatibility with thermodynamics then leads to the equations governing the extended set of state variables. The main limitation of this approach stems from the limitation in the mathematical formulation of the compatibility with thermodynamics. The mathematical formulation is limited to equations that are linear in the newly adopted state variable. We can regard thus the *GENERIC* approach followed in this paper as a non linear extension of extended irreversible thermodynamics (see also Refs. [23, 24]).

Before proceeding to complex fluids we shall briefly continue the discussion of the nonstandard diffusion in simple fluids by focusing on the spatial inhomogeneities. We shall extend Eqs. (4.38)-(4.41) to governing equations of a weakly non-local theory.

4.6.2. Weakly non-local diffusion in simple fluids

If the spatial inhomogeneity is relevant then, following Cahn and Hilliard [25], the free energy Φ will be a spatially non-local function (i.e. of the form $\Phi = \int d\mathbf{r} \int d\mathbf{r}' \varphi(\mathbf{r}, \mathbf{r}')$). As a special case, when $\varphi(\mathbf{r}, \mathbf{r}')$ is strongly peaked at $\mathbf{r} = \mathbf{r}'$, we can approximate the fully non local free energy by one that is still a local function but involves also derivatives with respect to $\mathbf{r}$. We shall here work out only the case when Φ contains an extra term

$$B \int d\mathbf{r}\ \partial_\alpha c\, \partial_\alpha c \tag{4.54}$$

where B is a constant. This term has also been considered in the rheology-diffusion coupling in Ref. [3]. In general, of course, we should include terms involving gradients of

w and **u**. A remarkable advantage of the *GENERIC* formulation is that we can easily extend the governing equations Eqs. (4.38)-(4.41) to the weakly non-local case (i.e. with the free energy involving the new term (4.54)). What we have to do only is to replace the Volterra derivative $\delta\Phi/\delta c$ by a variational Volterra derivative, i.e.

$$\frac{\delta \Phi}{\delta c} \quad \rightarrow \quad \frac{\delta \Phi}{\delta c} - \partial_\gamma \frac{\delta \Phi}{\delta (\partial_\gamma c)} \tag{4.55}$$

If Φ would involve terms with gradients of **w** and **u** then we would correspondingly change the derivative Φ_w and Φ_u. The Poisson kinematics remains the same. There may be introduced new terms in the dissipation bracket but since we let it depend only on Φ_u and Φ_w we leave it unchanged.

After a straightforward calculation we arrive at Eqs. (4.38)-(4.41) but the extra stress tensor is modified as follows

$$\tau_{\alpha\gamma} = \tau_{\alpha\gamma}^{(4.45)} + (\partial_\alpha c)(\Phi_{\partial_\gamma c}) \tag{4.56}$$

where $\tau_{\alpha\gamma}^{(4.45)}$ is the stress tensor given by Eq. (4.45). The new second term on the right hand side of (4.56) was also found in the Ref. [3]. It is important to note that in our analysis the extra stress tensor proportionnal to $\partial_\alpha(c)\partial_\beta(c)$ is already included in $\tau_{\alpha\gamma}^{(4.45)}$. In other words, in the context of our analysis, the elastic extra stress tensor proportionnal to $\partial_\alpha(c)\partial_\beta(c)$ arises even if the free energy does not include the term (4.54). A new term is also present in the osmotic pressure

$$\pi_i = \pi_i^{(4.48)} + \partial_\alpha(\rho_i)\,\tilde{\varphi}_{i\partial_\alpha\rho_i} \qquad i = 1, 2 \tag{4.57}$$

$\pi_i^{(4.48)}$ is the osmotic pressure given by (4.48). Because of the diffusion-rheology coupling, weak nonlocality will influence both rheology and diffusion. Should we allow Φ

to depend also on $\partial_\gamma w_\alpha$ then new terms would also arise in p, π and τ and in Eqs. (4.40) and (4.41). For example, the diffusion flux will no longer be given by (4.47) but rather by

$$J_\alpha = \rho c(1-c)\left(\Phi_{w_\alpha} - \partial_\gamma \Phi_{\partial_\gamma w_\alpha}\right) \tag{4.58}$$

Also Eq. (4.41) will contain an extra term. Both rheology and diffusion are thus modified if Φ is let to depend on gradients of c and w.

4.7. Diffusion with Inertia in Complex Fluids

In this section, we look for a realization of Eq. (4.27) that corresponds to a binary mixture with one component (the first one) being a simple fluid (solvent) and the second one being a complex (e.g. polymeric) fluid. The two components are assumed to be fully miscible. We choose to characterize our system with the state variables (4.6) or (4.9). We thus look for two realizations of Eq. (4.27), one with (4.6) as state variables and one with (4.9) as state variables. The Poisson kinematics in both cases has been found in (4.22) and (4.24). We proceed now to the determination of the dissipation bracket. Following the experience collected in the study of polymeric fluids [26, 27] we suggest:

$$[A, B] = \int dr \int dR \, \frac{\partial}{\partial R_\gamma}\left(A_\psi\right)\frac{\Gamma}{2}\psi \, \frac{\partial}{\partial R_\gamma}\left(B_\psi\right) + \int dr \, A_{w_\alpha}\frac{\Lambda}{2} B_{w_\alpha} \tag{4.59}$$

if the state variables (4.6) are used, and

$$[A, B] = \int dr \, A_{m_{\alpha\beta}} \frac{K}{2} m_{\beta\gamma} B_{m_{\gamma\alpha}} + \int dr \, A_{w_\alpha}\frac{\lambda}{2} B_{w_\alpha} \tag{4.60}$$

if the state variables (4.9) are used. The quantities Γ, Λ, K, λ are considered to be phenomenological parameters. In order to satisfy the general requirement (4.28) they all have to be positive. They can however also depend on state variables. If we compare the dissipation brackets (4.59), (4.60) with the dissipation bracket (4.34) introduced in the

context of simple fluids, we note that we use the same terms to express the dissipation of w but we do not use in the context of complex fluids any Navier-Stokes-like direct dissipation of the momentum u. Instead, we let to dissipate directly only the polymeric structure. We shall see later that this dissipation then indirectly (i.e. in the process of solving the governing equations) brings about the Navier -Stokes-like dissipation obtained in Section 5.6.

Now we have collected all the elements of the *GENERIC* structure (except for the free energy that will remain undetermined) and we can thus write explicitly the corresponding realizations of Eq. (4.27). The same type of calculations as those that led us to (4.38)-(4.41) lead us now to :

$$\frac{\partial \rho}{\partial t} = \left(\frac{\partial \rho}{\partial t}\right)^{(0)} \tag{4.61}$$

$$\frac{\partial u_\alpha}{\partial t} = \left(\frac{\partial u_\alpha}{\partial t}\right)^{(0)} \tag{4.62}$$

$$\frac{\partial c}{\partial t} = \left(\frac{\partial c}{\partial t}\right)^{(0)} \tag{4.63}$$

$$\frac{\partial w_\alpha}{\partial t} = \left(\frac{\partial w_\alpha}{\partial t}\right)^{(0)} + \left(\frac{\partial w_\alpha}{\partial t}\right)^{(1)} \tag{4.64}$$

$$\begin{aligned}\frac{\partial \psi}{\partial t} = & - \partial_\gamma\left(\psi \Phi_{u_\gamma}\right) - \frac{\partial}{\partial R_\alpha}\left(\psi R_\gamma \partial_\gamma \Phi_{u_\alpha}\right) \\ & + \partial_\gamma\left(c\psi \Phi_{w_\gamma}\right) + \frac{\partial}{\partial R_\alpha}\left(\psi R_\gamma \partial_\gamma\left(c\Phi_{w_\alpha}\right)\right) \\ & + \frac{\partial}{\partial R_\alpha}\left(\Gamma\psi \frac{\partial}{\partial R_\alpha}\left(\Phi_\psi\right)\right)\end{aligned} \tag{4.65}$$

if the state variables (4.6) are used. In Eqs. (4.61)-(4.64) we use the symbol $\left(\frac{\partial}{\partial t}\right)^{(0)}$ to denote the terms given by Eqs. (4.38)-(4.41). In Eq. (4.62) the scalar hydrodynamic pressure p reads as

$$p = -\varphi + \rho\varphi_{\rho} + u_{\alpha}\varphi_{u_{\alpha}} + w_{\alpha}\varphi_{w_{\alpha}} + \int d\mathbf{R}\,\psi\,\Phi_{\psi} \tag{4.66}$$

and the extra stress tensor by

$$\tau_{\alpha\gamma} = \tau_{\alpha\gamma}^{d.e.} - \tau_{\alpha\gamma}^{p} \tag{4.67}$$

where $\tau_{\alpha\gamma}^{d.e.}$ is given by (4.46) and

$$\tau_{\alpha\gamma}^{p} = \int d\mathbf{R}\,\psi\,R_{\alpha}\frac{\partial}{\partial R_{\gamma}}\left(\Phi_{\psi}\right) \tag{4.68}$$

In Eq. (4.64), $\left(\frac{\partial w_{\alpha}}{\partial t}\right)^{(0)}$ stands for the right hand side of (4.41) except for the last two terms. While the solvent osmotic pressure remains the same as in Eq. (4.48), the polymer expression contains the contribution of its internal structure

$$\pi_{p} = -\bar{\varphi}_{p} + \rho_{p}\,\bar{\varphi}_{p\rho_{p}} + w_{\gamma}\bar{\varphi}_{pw_{\gamma}} + \int d\mathbf{R}\psi\Phi_{p\psi} \tag{4.69}$$

$\bar{\varphi}_{p}$ is the free energy density with u_{s} and ρ_{s} fixed (the subscript s designates the solvent). The term $\left(\frac{\partial w_{\alpha}}{\partial t}\right)^{(1)}$ in Eq. (4.64) stands for

$$\left(\frac{\partial w_{\alpha}}{\partial t}\right)^{(1)} = -c\partial_{\gamma}\tau_{\alpha\gamma}^{p} - \Lambda\Phi_{w_{\alpha}} \tag{4.70}$$

In the case of the state variables (4.9) we end up with the same equations (4.61)-(4.64) except that (4.66) is replaced by

$$p = -\varphi + \rho\varphi_{\rho} + u_{\alpha}\varphi_{u_{\alpha}} + w_{\alpha}\varphi_{w_{\alpha}} + m_{\alpha\beta}\varphi_{m_{\alpha\beta}} \tag{4.71}$$

the elastic extra stress tensor τ^{p} is given by

$$\tau^{p}_{\alpha\gamma} = 2m_{\alpha\beta}\frac{\delta\Phi}{\delta m_{\beta\gamma}} \tag{4.72}$$

the polymer osmotic pressure (4.69) becomes

$$\pi_{p} = -\hat{\varphi}_{p} + \rho_{p}\hat{\varphi}_{p\rho_{p}} + w_{\gamma}\hat{\varphi}_{pw_{\gamma}} + m_{\alpha\beta}\hat{\varphi}_{pm_{\alpha\beta}} \tag{4.73}$$

and

$$\left(\frac{\partial w_{\alpha}}{\partial t}\right)^{(1)} = -c\partial_{\gamma}\tau^{p}_{\alpha\gamma} - \lambda\Phi_{w_{\alpha}} \tag{4.74}$$

The equation governing the time evolution of the polymeric structure (characterized by the conformation tensor **m**) is now

$$\begin{aligned}\frac{\partial m_{\alpha\beta}}{\partial t} = &-\partial_{\gamma}\left(m_{\alpha\beta}\Phi_{u_{\gamma}}\right) + m_{\gamma\beta}\partial_{\gamma}\Phi_{u_{\alpha}} + m_{\gamma\alpha}\partial_{\gamma}\Phi_{u_{\beta}} \\ &+ \partial_{\gamma}\left(cm_{\alpha\beta}\Phi_{w_{\gamma}}\right) - m_{\gamma\beta}\partial_{\gamma}\left(c\Phi_{w_{\alpha}}\right) - m_{\gamma\alpha}\partial_{\gamma}\left(c\Phi_{w_{\beta}}\right) - 2Km_{\beta\gamma}\Phi_{m_{\gamma\alpha}}\end{aligned} \tag{4.75}$$

The physical interpretation of the new terms that arise in the context of complex fluids will be revealed below in the analysis of solutions of the governing equations. Here we only note that the equations governing the time evolution of the polymeric structure (i.e. Eqs. (4.65) and (4.75)) are a natural extension of the equations that arise in one-component analysis of polymeric fluids. The new in Eq. (4.65) are the third and fourth terms on the right hand side expressing the convection (in both **r** and **R**) due to the

presence of the diffusion flux. The new terms playing this role in Eq. (4.75) are the fourth, fifth and sixth terms on the right hand side.

4.7.1. Properties of solutions of Eqs. (4.61)-(4.65)

As in the previous section we first look at solutions for $t \to \infty$. Since the governing equations are particular realizations of *GENERIC* (Eq. (4.27)) we know again that as $t \to \infty$ solutions to (4.61) - (4.65) (or (4.61) - (4.64), (4.75)) approach equilibrium states that are the states for which the free energy Φ is minimum. The equilibrium thermodynamics relation implied by Eqs. (4.61)-(4.65) is specified by Φ evaluated at the equilibrium state.

Next, we examine the approach to equilibrium. At this stage we can assume that the polymeric structure (characterized either by ψ or $\mathbf{m}$) and $\mathbf{w}$ are already almost equilibrated so that we can put $\partial\psi/\partial t \approx 0$. By neglecting terms that become small, we obtain from Eq. (4.65)

$$\frac{\partial}{\partial R_\alpha}\left(-\psi R_\gamma \partial_\gamma \Phi_{u_\alpha} + \psi R_\gamma \partial_\gamma\left(c\Phi_{w_\alpha}\right) + \Gamma\psi \frac{\partial}{\partial R_\alpha}\left(\Phi_\psi\right)\right) = 0 \tag{4.76}$$

and

$$+ m_{\gamma\beta}\partial_\gamma \Phi_{u_\alpha} + m_{\gamma\alpha}\partial_\gamma \Phi_{u_\beta} - m_{\gamma\beta}\partial_\gamma\left(c\Phi_{w_\alpha}\right) - m_{\gamma\alpha}\partial_\gamma\left(c\Phi_{w_\beta}\right) - 2Km_{\beta\gamma}\Phi_{m_{\gamma\alpha}} = 0 \tag{4.77}$$

from Eq. (4.75). From (4.76) and using (4.68) we have

$$\tau^p_{\alpha\beta} = \frac{1}{\Gamma}\left(\int d\mathbf{R} R_\alpha R_\gamma \psi\right)\partial_\gamma\left(\Phi_{u_\beta}\right) - \frac{1}{\Gamma}\left(\int d\mathbf{R} R_\alpha R_\gamma \psi\right)\partial_\gamma\left(c\Phi_{w_\beta}\right) \tag{4.78}$$

Similarly, we can derive from (4.76) and (4.72)

$$\tau^p_{\alpha\beta} = \frac{1}{K}\left(m_{\gamma\beta}\partial_\gamma\left(\Phi_{u_\alpha}\right) + m_{\gamma\alpha}\partial_\gamma\left(\Phi_{u_\beta}\right)\right) - \frac{1}{K}\left(m_{\gamma\beta}\partial_\gamma\left(c\Phi_{w_\alpha}\right) + m_{\gamma\alpha}\partial_\gamma\left(c\Phi_{w_\beta}\right)\right) \tag{4.79}$$

If we compare the total extra stress tensor (4.67) with the total stress tensor (4.46) that has arisen in simple fluids, we recover the classical Navier-Stokes-like terms (now

however with anisotropic viscosity coefficients) as well as the terms expressing the resistance to gradients of the diffusion velocity Φ_w.

Now we turn our attention to Eq. (4.64). At the final stage of the approach to equilibrium we put $\partial w/\partial t \approx 0$ and obtain from (4.64) and (4.70) (respectively (4.74))

$$-\Lambda \Phi_{w_\alpha} - c\partial_\gamma \tau^p_{\alpha\gamma} - \rho c(1-c)\partial_\alpha\left(\frac{\Phi_c}{\rho}\right) = 0 \tag{4.80}$$

and thus

$$\Phi_{w_\alpha} = \left(\Phi_{w_\alpha}\right)^{Fick} - \frac{c}{\Lambda}\partial_\gamma \tau^p_{\alpha\gamma} \tag{4.81}$$

where $\left(\Phi_{w_\alpha}\right)^{Fick}$ is given by (4.50). If we insert (4.81) into (4.63) we obtain

$$\frac{\partial c}{\partial t} = -\Phi_{w_\alpha}\partial_\alpha(c) + \frac{1}{\rho}\partial_\alpha\left[\frac{(\rho c(1-c))^2}{\Lambda}\partial_\alpha\left(\frac{\Phi_c}{\rho}\right) + \frac{\rho c^2(1-c)}{\Lambda}\partial_\gamma \tau^p_{\gamma\alpha}\right] \tag{4.82}$$

If the state variables (4.9) are used then we also arrive in this way to (4.81) and (4.82) except that Λ is replaced by λ. Equation (4.82) is the diffusion equation found in many previous studies of diffusion in polymeric fluids [11-25, 28, 35-42]. The new contributions that we are bringing in this paper are two-fold :

(i) The coupling between rheology and diffusion is expressed within a systematic and complete framework called a GENERIC formalism. Equation (4.82) is only an approximate solution, representing the final stage of the approach to equilibrium, of the complete set of equations (4.61)-(4.65).

(ii) Besides the influence of the stresses on diffusion (expressed for instance in Eq. (4.82)) we also reveal the influence of diffusion on stresses expressed in Eqs. (4.65), (4.68) or (4.75), (4.72).

4.8. Conclusion

The main result of this paper is a family of Eqs. (4.61)-(4.75) describing diffusion and rheology in the isothermal mixture composed of one simple and one complex fluids. The family is parameterized by two types of quantities : one is the free energy Φ and the other are the kinetic coefficients entering the dissipation bracket (either Eqs.(4.61)-(4.75) provide a setting that unifies previous formulations and extend them to a more detailed and complete analysis. What are the experimental observations with which we compare our theoretical formulation?

First it is the observation that in the absence of external forces the mixture reaches eventually an equilibrium state at which its behavior is found to be well described by equilibrium thermodynamics. This result is indeed implied, as we have seen by Eqs. (4.61)-(4.75) for any set of equations in the family. Moreover, we have seen that the fundamental equilibrium thermodynamics relation implied by Eqs. (4.61)-(4.75) is the one specified by the free energy Φ evaluated at the equilibrium state (a state reached as $t \rightarrow \infty$). We emphasize that this fundamental agreement is very rarely checked in other approaches.

The second experimental observation with which we have compared Eqs. (4.61)-(4.75) is the observation that the diffusion in the mixture that is not too far from equilibrium is well described by either Eq. (4.82) or by classical Fickean diffusion (consequence of the diffusion equation of the type Eq. (4.82) have been extensively compared with detailed experimental observations in the literature). This comparison we make again before specifying the free energy Φ and the coefficients entering the dissipation bracket.

Other effects that are predicted by our formulation and not by other formulations remain in this paper only qualitative since we do not embark on the task of specifying the free energy and the kinetic coefficients entering dissipation brackets. The new predictions concern mainly the influence of diffusion on rheology. The systematic analysis presented in

this paper treats both sides of the coupling (i.e. the influence of rheology on diffusion, studied extensively in the past, and the influence of diffusion on rheology) on the same footing. The new type of the influence of the diffusion on rheology we see in the term Eq. (4.46) that combines with the classical term Eq. (4.68) to give the extra stress tensor Eq.(4.67).

Although the case of two simple fluids is investigated mainly for the sake of being systematic it was nevertheless found that diffusion-rheology coupling may be of interest even in the context of simple fluids. If the mixture is inhomogeneous (in composition as well as in flow) it is shown that the diffusion is, in general, non-Fickean and the rheology becomes complex (viscoelastic). We do not know about any experimental observations of diffusion and rheology in strongly inhomogeneous mixtures of two simple fluids that could be compared with our qualitative predictions. In the more complicated situation of one simple and one complex fluid (e.g. a polymer solution) we recover the well known diffusion equation involving the stresses and we have established a new rheological equation of state in which the diffusion flux is involved. The main contribution to be expected by a *GENERIC* analysis is a better comprehension of the diffusion-rheology coupling.

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4.9. References

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CHAPITRE 5

NON-FICKIAN MASS TRANSPORT IN POLYMERS. I

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5.1. Abstract

When a solvent penetrates a polymeric medium, the medium cooperates. The polymeric macromolecules continuously rearrange themselves to accommodate the solvent molecules. The participation of the medium brings inertia into the diffusion process. In classical models, the inertia is expressed in the coupling of the time evolution of the solvent concentration to the time evolution of the polymeric structure. In this paper, we add also coupling to the time evolution of the diffusion flux. From the physical point of view, this extension renders the model more realistic. From the mathematical point of view, the extended model becomes simpler (the governing equations are more numerous but they are first order partial differential equations and thus simpler than the governing equations of the classical models). For example, the observed shock-wave type propagation of the solvent appears to be one of their typical solutions. In this paper, we derive the governing equations of the new extended model, investigate how the previously introduced models (as e.g. the Fickian model or the classical Case II model) arise as its particular cases, and investigate in detail (both from the analytical and the numerical point of view) one simplified version of the extended model in which the only extra independent state variable is the diffusion flux (the polymeric structure is thus expressed in it indirectly in terms of the diffusion flux). The governing equations of the simplified model are similar to the governing equations of the isothermal compressible simple fluid. Many properties of solutions as well as numerical methods to calculate them in detail are thus immediately available. The calculated and the experimentally observed (taken from the literature) time evolutions of the solvent concentration are found to be in agreement. In particular, the model predicts the experimentally observed shock-wave type propagation of the solvent also in the absence of the glass-rubber transition.

5.2. Introduction

If a solvent and a dry polymer film come into contact then the solvent starts to penetrate the film. Three types of the sorption process have been observed [Alfrey et al. (1966)]: (i) Fickian diffusion in which the mass of the absorbed solvent $m_s \approx t^{1/2}$ (t denotes the time). (ii) Case II diffusion in which, after an induction time, $m_s \approx t$, moreover, the moving boundary separating the swollen and the dry polymer is sharp (Alfrey shock waves). (iii) An anomalous diffusion (a combination of (i) and (ii) above). The basic physics that is behind the observed deviations from the classical Fickian diffusion has been understood for a long time. In order for the solvent to enter the polymer, the polymer has to rearrange itself. The changes in the conformation arising due to these rearrangements create then internal stresses in the polymer. Consequences of such stresses (e.g. creation of crazes) have indeed been observed [Alfrey et al. (1966), Thomas et al. (1981)]. From a qualitative viewpoint [Vrentas et al. (1975, 1977)], the three types of the sorption process correspond, roughly speaking, to the three types of the relation between the characteristic time scale τ_d of the penetration and the characteristic time scale τ_p of the changes of the polymer structure. The Fickian diffusion occurs when $\tau_p \ll \tau_d$, Case II diffusion occurs when $\tau_p \gg \tau_d$ and the anomalous diffusion occurs when $\tau_p \approx \tau_d$. A more detailed picture will arise later in this paper and in the accompanying paper that we shall refer to as Part II.

Since the polymer structure plays such an important role in nonstandard diffusion processes, their theoretical analysis has to address the time evolution of both the solvent concentration and the polymer structure. The polymer structure can be taken into account in the theoretical descriptions either explicitly (Sections 5.3, 5.4 and Part II) or implicitly (Sections 5.5., 5.6).

In the first models of Case II diffusion [Thomas et al. (1982), Durning. et al. (1986), Wu et al. (1993)] (we shall call them here classical Case II models), the polymer structure is characterized indirectly by the extra stress tensor whose time evolution is assumed to be governed by the equation arising in the Maxwell rheological model [Durning. et al.

(1986), Wu et al. (1993)]. To express the changes in the polymer structure that may take place during the diffusion process (for example glass-rubber transitions, polymer swelling, etc) the parameters entering the Maxwell model are let to depend appropriately on the solvent concentration. The diffusion is coupled to the equation governing the time evolution of the extra stress tensor by requiring the Fickian diffusion to be compatible with thermodynamics. A well known consequence of this requirement is that the diffusion flux is proportional to the gradient of the chemical potential rather than just to the gradient of the concentration. Since the chemical potential depends on the concentration and also on the internal structure of the polymer (and thus on the extra stress tensor that plays in this model the role of the state variable characterizing it), the diffusion flux is proportional to the gradient of both the concentration and the extra stress tensor. Classical Case II models represent an important progress in the theoretical investigation of the nonstandard diffusion. In this and the accompanying paper we follow [El Afif et al (1999)] and extend this investigation towards a more realistic rheology and a more systematic discussion of Alfrey shocks (including for example those that are not accompanied with the glass-rubber transitions, [Thomas et al. (1978, 1981), Barriere (1997)])

Experience collected in rheological modeling shows clearly that a single rheological model for all polymeric materials and all situations does not exist. The way the polymeric structure is represented in theoretical analysis depends both on the polymer itself and on the information that we want to obtain from the analysis. The best way to see a rheological model is as a family of mutually compatible models formulated on a hierarchy of levels of description. In [El Afif et al. (1999)], we have introduced such family for analyzing the coupling of rheology and diffusion in solvent-polymer mixtures. The polymeric structure is chosen to be characterized by the configuration distribution function or a conformation tensor $\mathbf{m}(\mathbf{r})$, where $\mathbf{r}$ denotes the position coordinate. The individual features of the solvent and the polymer are expressed in the free energy and in the dissipation potential. These quantities parameterize the models in the family. The mutual compatibility is guaranteed by the fact that all the models in the family are

realizations of the unifying GENERIC structure [Grmela et al. (1997), Oettinger et al. (1997)]. This then also implies that solutions of their governing equations agree with results of the experimental observations that constitute the experimental basis of equilibrium thermodynamics (externally unforced systems are seen to reach states at which their behavior is found to be well described by equilibrium thermodynamics).

In this and in the accompanying paper (see chapter 6), we continue to investigate predictions implied by the family of models introduced in [El Afif et al. (1999)]. Besides their compatibility with equilibrium thermodynamics, we turn our attention also to other more detailed properties of solutions to their governing equations. First however, we narrow down our investigation to the sorption (penetration) in the absence of overall flow and in the overall mechanical equilibrium. The governing equations derived in [El Afif et al. (1999)] reduce in these special circumstances to the governing equations appearing in Section 5.3. The theoretical formulation arising in Section 5.3 will be called a (c,**w**,**m**)-model since the polymer concentration c, the diffusion flux **w** and the conformation tensor **m** play in it the role of independent state variables. In Sections 5.3-5.6 as well as in Part II (chapter 6), we then investigate solutions to the governing equations of (c,**w**,**m**)-model. The investigation consists of: (i) a comparison with implications of other theoretical descriptions, (ii) analytical and numerical investigations that include investigations of the wave propagation, and (iii) a comparison with results of experimental observations. In this paper, we focus our attention on the confrontation with other well known or new reduced theoretical descriptions. By a reduced theoretical description, we mean a model in which some of the state variables (c, **w**, **m**) become dependent state variables (i.e. they are lost from the time evolution equations but they are not lost from the analysis; they remain in the form of formulas expressing them in terms of the independent state variables). The analysis leads to: (i) the well known Fickian model (Section 5.5), called here a c-model since the only independent state variable in it is the solvent concentration c, (ii) a model, called a **m**-model (Section 5.4.1), describing the diffusion of disturbances in the polymer, (iii) a new model (Section 5.6), called a (c,**w**)-model, that describes in a very simple way the experimentally observed Case II

diffusion (Alfrey shock waves), (iv) an extension of the classical Case II models (Section 5.4). The investigation of the new (c,w)-model is then carried further. Solutions of its governing equations are studied both analytically and numerically. They are then compared with predictions based on the Fickian description and with some experimental observations reported in the literature. In Part II, a similar type of analysis is done for (c,w,m)-model.

5.3. Model Derivation: (c,w,m)-model

As in [El Afif et al. (1999)], the systems that we consider in this paper are composed of a solvent (a simple fluid) and a polymer. These two component systems are assumed to be kept under a constant temperature. Following the two-fluid point of view [De Gennes (1976), Brochard et al. (1977), Doi (1983)] the solvent and the polymer are regarded as two fluids, each having its own mass density and its own momentum. In addition, the polymer is considered as a complex fluid whose internal structure has to be also taken into account. States of the solvent are thus chosen to be characterized by $(\rho_s, \mathbf{u}_s)$, denoting the fields of mass and momentum densities respectively, and states of the polymer by $(\rho_p, \mathbf{u}_p, \mathbf{m}_p)$ denoting the fields of mass density, momentum density and the conformation tensor respectively. Consequently, the state variables of the whole system are

$$(\rho, c, \mathbf{u}, \mathbf{w}, \mathbf{m}) \tag{5.1}$$

where $\rho = \rho_s + \rho_p$, $\mathbf{u} = \mathbf{u}_s + \mathbf{u}_p$, $c = \frac{\rho_s}{\rho_s + \rho_p}$, $\mathbf{w} = \frac{\rho_p}{\rho_s + \rho_p}\mathbf{u}_s - \frac{\rho_s}{\rho_s + \rho_p}\mathbf{u}_p$, $\mathbf{m} = \mathbf{m}_p$. An application of GENERIC [Grmela et al. (1997), Oettinger et al. (1997)] has led in [El Afif et al. (1999)] to equations governing the time evolution of (5.1). These equations are in fact a family of equations parameterized by the Helmholtz free energy Φ, and the

dissipation potential Ψ. It is in Φ and Ψ where the individual features of the physical systems under consideration are expressed. We recall that due to the fact that the governing equations are realizations of the mathematical structure collected in GENERIC, their solutions are guaranteed to agree with the observed compatibility with thermodynamics (isolated systems are observed to approach states at which their behavior is seen to be well described by equilibrium thermodynamics).

The two-fluid point of view of diffusion has also been followed by using other formulations of the compatibility with thermodynamics. For example, the formulation developed in the Extended Irreversible Thermodynamics has been used in [Neogi (1983), Jou et al. (1993), Manero et al (1999)].

In this paper, we narrow down our attention to the following special situation. We regard the polymer and the solvent in the coordinate system in which the overall momentum equals zero, i.e.

$$\mathbf{u} = 0 \tag{5.2}$$

and under overall mechanical equilibrium, i.e.

$$\partial_\alpha p + \partial_\gamma \sigma_{\alpha\gamma}^{(\text{overall})} \equiv 0 \tag{5.3}$$

where p is the scalar pressure, $p = -\tilde{\varphi} + \rho\Phi_\rho + w_\alpha \Phi_{w_\alpha} + m_{\alpha\beta}\Phi_{m_{\alpha\beta}}$, $\tilde{\varphi}$ is the density of the free energy Φ, i.e. $\Phi = \int d\mathbf{r}\tilde{\varphi}$, and $\sigma^{(\text{overall})}$ is the overall extra stress tensor, $\sigma_{\alpha\beta}^{(\text{overall})} = w_\alpha \Phi_{w_\beta} - \sigma_{\alpha\beta}^{(\text{polymer})}$; $\Phi_{\rho(\mathbf{r})} := \dfrac{\partial\Phi}{\partial\rho(\mathbf{r})}$, similarly $\Phi_{w_\alpha(\mathbf{r})}, \Phi_{c(\mathbf{r})}, \ldots$; $\partial_\alpha := \dfrac{\partial}{\partial r_\alpha}$; $\alpha,\beta,\gamma = 1,2,3$; and the summation convention is used. Under the constraint (5.2) the governing equations introduced in [El Afif et al. (1999)] become

$$\rho\frac{\partial c}{\partial t} = -\partial_\alpha\left(\rho c(1-c)\Phi_{w_\alpha}\right)$$

$$\frac{\partial w_\alpha}{\partial t} = -\partial_\beta\left((1-c)w_\alpha\Phi_{w_\beta}\right) - \rho c(1-c)\partial_\alpha\left(\frac{\Phi_c}{\rho}\right) + w_\gamma\partial_\alpha\left(c\Phi_{w_\gamma}\right) - (1-c)w_\gamma\partial_\alpha\Phi_{w_\gamma}$$
$$+ c\partial_\gamma\left(w_\alpha\Phi_{w_\gamma}\right) + cm_{\gamma\beta}\partial_\alpha\Phi_{m_{\gamma\beta}} - 2c\partial_\gamma\left(m_{\alpha\beta}\Phi_{m_{\gamma\beta}}\right) - \Lambda\Phi_{w_\alpha}$$

$$\frac{\partial m_{\alpha\beta}}{\partial t} = \partial_\gamma\left(c\, m_{\alpha\beta}\Phi_{w_\gamma}\right) - m_{\gamma\beta}\partial_\gamma\left(c\Phi_{w_\alpha}\right) - m_{\alpha\gamma}\partial_\gamma\left(c\Phi_{w_\beta}\right) - 2\lambda m_{\alpha\gamma}\Phi_{m_{\gamma\beta}} \qquad (5.4)$$

We recall that in (5.4) the dissipation potential Ψ has already been chosen to be a quadratic potential involving two phenomenological parameters Λ and λ. The dissipation potential Ψ possesses the properties required in GENERIC provided Λ and λ are real valued functions of the state variables and $\Lambda>0$, $\lambda>0$. We shall specify them more in Section 5.7. Application of the constraint (5.3) together with the partial specification of the free energy

$$\Phi(\rho_s, u_s, \rho_p, u_p, m) = \int dr\left(\frac{u_s^{\,2}}{2\rho_s} + \frac{u_p^{\,2}}{2\rho_p}\right) + \int dr\,\varphi\left(\rho_s, \rho_p, m\right) \qquad (5.5)$$

and the requirement of the overall incompressibility

$$\rho = const. \qquad (5.6)$$

lead then to

$$\frac{\partial c}{\partial t} = -\partial_\alpha\left(\frac{w_\alpha}{\rho}\right)$$

$$\frac{\partial w_\alpha}{\partial t} = -\partial_\beta\left(\frac{w_\beta w_\alpha}{\rho c}\right) - c\partial_\alpha\Phi_c - \frac{\Lambda}{\rho c(1-c)}w_\alpha \qquad (5.7)$$

$$\frac{\partial m_{\alpha\beta}}{\partial t} = \partial_\gamma\left(m_{\alpha\beta}\frac{w_\gamma}{\rho(1-c)}\right) - m_{\gamma\beta}\partial_\gamma\left(\frac{w_\alpha}{\rho(1-c)}\right) - m_{\alpha\gamma}\partial_\gamma\left(\frac{w_\beta}{\rho(1-c)}\right)$$
$$-\lambda(m_{\alpha\gamma}\varphi_{m_{\gamma\beta}} + m_{\beta\gamma}\varphi_{m_{\alpha\gamma}})$$

This system of the time evolution equations is completed by the formula

$$\sigma_{\alpha\beta}^{(polymer)} = 2m_{\alpha\gamma}\varphi_{m_{\gamma\beta}} \tag{5.8}$$

expressing the polymer extra stress tensor $\sigma^{(polymer)}$ in terms of the state variables (c, **m**). For sake of simplicity, the superscript (polymer) in Eq.(5.8) will be omitted in the following. In order to calculate this extra stress tensor, we thus have to solve (5.7) and then insert the solution into (5.8). Two comments concerning (5.5) and (5.8) are in order.

In the partial specification (5.5) of the free energy Φ, the first term represents the kinetic energy. The rest, i.e. the second term on the right hand side of (5.5), is the part of the free energy that is independent of the velocity. By φ we denote its density. In view of (5.2) and the transformation (5.1), the kinetic energy equals $\int dr \frac{w^2}{2\rho c(1-c)}$. This then implies that the mass flux density $\rho c(1-c)\Phi_w$ (see the first equation in (5.5)) coincides exactly with the relative momentum density **w**.

The second comment is about (5.8). The deformations in the polymer occurring in the diffusion process induce in it internal extra stresses. We can easily verify that the first and the second equations in (5.7) become, if transformed into the variables $\rho_p=\rho(1\text{-}c)$, $\tilde{\mathbf{u}}_p = -\frac{\mathbf{w}}{c}$ and $\mathbf{m} = \mathbf{m}$, the standard equations governing the time evolution of the mass density and the conformation tensor **m** of a polymeric fluid subjected to the flow $\tilde{\mathbf{u}}_p$. The internal extra stress tensor σ responding to $\tilde{\mathbf{u}}_p$ is thus given by the standard formula (5.8).

We shall call the model represented by (5.7) a (c,w,m)-model since the independent state variables in it are (c, w, m). The family (5.7) of the time evolution equations involves three parameters (real valued functions of the state variables): φ, denoting the density of the part of the free energy that is independent of the velocity w, and two parameters Λ and λ that are proportional to the relaxations times of w and m respectively. It is in these parameters where we express the individual features of the system under consideration. The three dimensional space with coordinates (φ, λ, Λ) will be denoted by the symbol $\wp$ and called a parameter space. We regard (5.7) as a family of the time evolution equations parameterized by the points in the parameter space $\wp$.

The investigation of solutions to Eqs. (5.7) is organized as follows. First, we identify regions in the parameter space $\wp$ in which solutions to (5.7) can be well approximated by solutions to simpler (reduced) sets of equations (Sections 5.4-5.6). Solutions of one such reduced set of equations, representing a new model called a (c,w)-model, are then studied in detail. Solutions of the complete set (5.7) of the governing equations of the (c,w,m)-model will be studied in detail in Part II (chapter 6) of this series.

5.4. Diffusion with m-inertia: (c, m)-model

In classical mechanics, the position coordinates of particles evolve in time with inertia. This is because the position coordinates as well as the velocities of the particles play in the time evolution the role of independent state variables whose time evolution is governed by two equations. We can take the same view of the time evolution equations (5.7). The right hand side of the first equation in (5.7), i.e. the "velocity of c ", involves w whose time evolution equation involves another quantity m that itself evolves in time. We can say that c in (5.7) evolves with double inertia (since two variables are involved in the velocity of c). Before investigating (5.7) in its completeness, we shall look at the single-inertia diffusion obtained as approximations of (5.7). In this section, we shall study

the m-inertia (arising when Λ is large); and in Section 6, the w-inertia (arising when Λ is small)

If we are in the region of the parameter space $\wp$ in which Λ is large, then w evolves rapidly towards the equilibrium. We recall that at equilibrium $\Phi_w=0$ and thus $w = 0$ (see (5.5)). This means that if Λ is large, w evolves rapidly to $w = 0$. We can consider therefore the relative momentum w to be already close to the equilibrium (i.e. small) and assume also that $\frac{\partial w}{\partial t}\approx 0$. Consequently, the second equation in (5.7) is replaced by

$\frac{\Lambda}{\rho c(1-c)} w_\alpha + c\,\partial_\alpha \varphi_c = 0$, and equations (5.7) become

$$
\begin{aligned}
&\rho \frac{\partial c}{\partial t} = -\partial_\gamma w_\gamma \\
&w_\gamma = -\rho D\left(\partial_\gamma c + L_{\alpha\beta}\partial_\gamma m_{\alpha\beta}\right) \\
&\frac{\partial m_{\alpha\gamma}}{\partial t} = \partial_\beta\left(m_{\alpha\gamma}\frac{w_\beta}{\rho(1-c)}\right) - m_{\alpha\beta}\partial_\beta\left(\frac{w_\gamma}{\rho(1-c)}\right) - m_{\beta\gamma}\partial_\beta\left(\frac{w_\alpha}{\rho(1-c)}\right) \\
&\qquad - \lambda\left(m_{\alpha\beta}\varphi_{m_{\beta\gamma}} + m_{\gamma\beta}\varphi_{m_{\beta\alpha}}\right)
\end{aligned}
\tag{5.9}
$$

where

$$D(c,m) = \frac{c^2(1-c)\varphi_{cc}}{\Lambda}, \tag{5.10}$$

is the diffusion coefficient and

$$L_{\alpha\beta}(c,m) = \frac{\varphi_{cm_{\alpha\beta}}}{\varphi_{cc}} \tag{5.11}$$

is a second order tensor that measures the relative importance of the elastic and the mixing parts of the free energy. Both D and L depend on the solvent concentration c and on the polymer structure characterized by m; φ is introduced in (5.5). These coefficients

will be specified further in Section 5.7. By φ_{cc}, we denote the second derivative of φ with respect to c, similarly, φ_{cm} denotes the second derivative of φ with respect to c and $\mathbf{m}$. As we have already noted, w is the mass flux of the solvent and $(-w/\rho(1-c))$ is the velocity of the polymer. The third equation in (5.9) shows that it is the latter vector with which the conformation tensor $\mathbf{m}$ is advected. We see thus that the polymer internal structure moves in the opposite direction to the solvent leading to an extension of the polymer network. The right hand side of the third equation in (5.9) is a sum of two contributions, the reversible part that tends to swell the polymer, and the irreversible part that opposes the swelling. The degree of swelling is therefore determined, among others, by the competition between these two contributions.

Equations (5.8)-(5.11) are the governing equations of (c,$\mathbf{m}$)-model that we also refer to as an extended Case II model. A similar model has been introduced also in [Mavrantzas et al. (1992), Beris et al. (1994)]. If we assume that (5.8) can be solved for $\mathbf{m}$ (i.e. we assume that (5.8) represents a one-to-one relation between σ and $\mathbf{m}$), then the second equation in (5.9) can be replaced by the corresponding time evolution for the extra stress tensor σ. Equations (5.9) written in this form become the governing equations of classical Case II model provided the free energy φ is chosen to be the one representing the Maxwell rheological model and the nonlinear terms on the right hand side in the third equation are ignored. With this choice of φ, relation (5.8) becomes, indeed, a one-to-one relation between σ and $\mathbf{m}$ (see more in Part II, chapter 6).

What can we say about solutions to (5.9)? An extensive analytical investigation of solutions of a special case of (I.9), namely of the governing equations of the classical Case II model, has been carried out in [Edwards (1995), Edwards et al. (1995)]. In addition, their numerical solutions have also been extensively studied in [Fu et al. (1995), Wu et al. (1993)]. We shall make additional comments about solutions to (5.9) in Part II where we discuss solutions to the complete set (5.7) of the governing equations. In the following section, we shall identify regions in the parameter space $\wp$ in which the set of equations (5.9) can be further simplified.

5.4. 1. m-model

Disturbances in the polymer structure (e.g. formation of crazes) are sometimes seen to diffuse to other parts of the polymer. Equations (5.9) describe also this diffusion process. If **L** is large (we recall that by considering (5.9) instead of (5.7) we already assume that A is large) then we can neglect the first term on the right hand side of the second equation in (5.9) and arrive at

$$w_\gamma = -\rho_p E_{\alpha\beta}\partial_\gamma m_{\alpha\beta} \tag{5.12}$$

where $\rho_p = \rho(1-c)$ is the polymer density (see (5.1)) and **E** is related to **L** by $(1-c)\mathbf{E} = D\mathbf{L}$. Note that if **L** is negative then **E** is negative since $D>0$. By inserting (5.14) into the third equation in (5.9) we obtain

$$\frac{\partial m_{\alpha\gamma}}{\partial t} = -\partial_\beta\left(E_{\mu\theta}m_{\alpha\gamma}\partial_\beta m_{\mu\theta}\right) + m_{\alpha\beta}\partial_\beta\left(E_{\mu\theta}\partial_\gamma m_{\mu\theta}\right) + m_{\beta\gamma}\partial_\beta\left(E_{\mu\theta}\partial_\alpha m_{\mu\theta}\right) - 2\lambda m_{\alpha\beta}\varphi_{m_{\beta\gamma}} \tag{5.13}$$

The first equation in (5.9), written now as an equation describing the time evolution of the polymer concentration ρ_p, becomes

$$\frac{\partial \rho_p}{\partial t} = -\partial_\alpha\left(\rho_p E_{\beta\gamma}\partial_\alpha m_{\beta\gamma}\right) \tag{5.14}$$

The extra stress tensor σ, expressed as a function of **m**, determined by (5.13), is then given in (5.8). Equations (5.8), (5.12), (5.13) and (5.14) represent a model of the

diffusion of disturbances in the polymeric structure. We shall not pursue this model in this paper any further.

5.5. Diffusion without Inertia : c-model

The time evolution equations (5.9) can be replaced by simpler equations if **L** is either small or large. In the former case, we neglect the second term on the right hand side of the second equation in (5.9) and end up with the first equation in (5.9) that is decoupled from the rest of the equations. In the latter case we neglect the first term on the right hand side of the second equation in (5.9) and end up with the third equation in (5.9) that is decoupled from the rest of the equations. In the former case, it is diffusion of the solvent and in the latter case, it is diffusion of the changes in the structure of the polymer. Below, we shall discuss diffusion without inertia in a more detail.

We know from observations that if the polymer is replaced by a simple fluid or if the polymer is in the rubbery state in which deviations from equilibrium relax very rapidly, then the penetration of the solvent follows the Fick diffusion [Fick (1855)]. In this section, we shall see how and in what region of the parameter space $\wp$ the equations (5.9) reduce to the governing equations of the Fick diffusion. We shall also see what new information about the Fickian diffusion arises if the Fickian diffusion is regarded in the context of (5.9).

If Λ is large (this is the assumption that allowed us to reduce (5.7) to (5.9)) and **L** is small then the second equation in (5.9) reduces to the Fick first law

$$w_\gamma = -\rho D \partial_\gamma c \tag{5.15}$$

that, if substituted into the first equation in (5.9) (called also a Fick second law), leads to

$$\rho\frac{\partial c}{\partial t}=\partial_r\left(\rho D\partial_r c\right) \tag{5.16}$$

describing the time evolution of the solvent concentration. This equation remains still coupled to the third equation in (5.9) since the diffusion coefficient D depends, in general, on **m**. We shall now step out of the context of (c,w,m)-model (5.9) and regard (5.16) as an equation representing a new, more macroscopic, level of description on which states are described only by one scalar function, namely by the solvent concentration c. The diffusion coefficient D(c) (a real valued function of the solvent concentration c) is the only quantity in which we express on this level the individual features of the fluid under consideration. Its specification will be called a constitutive relation on the c-level of description. By viewing (5.16) in the context of (5.7) or (5.9) we gain, of course, an additional information. It is an information concerning the domain of validity of (5.16). On the c-level such information can be obtained only by making a comparison of theoretical predictions with results of experimental observations.

To make theoretical predictions based on (5.16) means to solve (5.16). A good review of properties of solutions of (5.16) can be found for example in [Crank (1956)]. It has been demonstrated that while many observed types of diffusion can be reproduced by choosing appropriately D(c), Case II and the anomalous diffusion are not among them. Less investigated are solutions to (5.16) in which the diffusion coefficient D is let to depend not only on c but also on gradients of c. The diffusion equation (5.13) then becomes a nonlinear partial differential equation involving the second and higher order derivatives. We shall not try in this paper to contribute to the knowledge about properties of solutions of this type of equations.

It is important to note that by arriving at the diffusion equation (5.16) from (5.7) or (5.9) we do not only obtain the diffusion equation (5.16) but we still keep the remaining two equations in (5.9) and also the expression (5.8) for the extra stress tensor. This then means that we still keep in touch with changes in the polymer structure and creation of extra stresses that accompany the diffusion process. By inserting the solution of the

diffusion equation (5.16) into the third equation in (5.9), we obtain an equation determining $\mathbf{m}$. We can solve it and obtain in this way the polymer structure that accompanies the Fickian diffusion. Together with (5.8) we then also obtain the associated with it extra stress tensor.

Finally, we recall from [El Afif et al. (1999)] that the extra stress tensor associated with the Fickian diffusion appears even in the setting in which the state variables characterizing the internal structure are completely ignored (i.e. on the c-level of description). It suffices to let the free energy depend also on the gradients of the solvent concentration. GENERIC structure then implies that the elastic part of the extra stress tensor equals $\partial_\alpha(c)\varphi_{\partial_\beta(c)}$.

5.6. Diffusion with w-inertia: (c, w)-model

So far, we have succeeded to simplify (5.7) by assuming that Λ is large. If Λ is small then we have to conclude that the three equations (5.7) cannot be further simplified. This is because in the most cases of practical interest, there is a strong coupling in φ between c and $\mathbf{m}$ (i.e. $\mathbf{L}$ is large) and the polymer structure relaxes relatively slowly (i.e. λ is not large). In Part II, we shall indeed embark on a systematic investigation of solutions to (5.7). There is still however one simpler and physically interesting set of governing equations that can be recognized in (5.7). Our objective in this section is to recognize it and then to analyze its solutions.

If Λ is small and λ large then we keep the second equation in (5.7) unchanged and solve approximately the third equation. This will give us the equation

$$\varphi_{m_{\alpha\beta}} = \frac{1}{\lambda}\left(\frac{1}{2}\delta_{\alpha\beta}\partial_\gamma\left(\frac{w_\gamma}{\rho(1-c)}\right) - \partial_\alpha\left(\frac{w_\beta}{\rho(1-c)}\right)\right) \tag{5.17}$$

that can be, in principle, solved for **m**. By inserting the solution of (5.17) (i.e. **m** as a function of c and **w**) into the second equation in (5.7) we end up with two equations governing the time evolution of c and **w**. Note that these equations will involve second and higher order derivatives with respect to **r**.

Now, we make the same step as we made in Section 5.4.1. We liberate ourselves from the context of (c,**w**,**m**)-model (5.7) and step up on a more macroscopic level of description. In Section 5.4.1 the more macroscopic level was the level on which states are characterized only by c. Here, the more macroscopic level is the level on which states are chosen to be described by c and **w**. As we see from (5.7), the governing equations on this level are:

$$\begin{aligned} \frac{\partial c}{\partial t} &= -\partial_\gamma\left(cv_\gamma\right) \\ \frac{\partial\left(cv_\alpha\right)}{\partial t} &= -\partial_\gamma\left(cv_\gamma v_\alpha\right) - \partial_\alpha\left(\frac{\pi}{\rho}\right) - \xi(c)v_\alpha \end{aligned} \tag{5.18}$$

where $\pi(c)$ is the osmotic pressure defined by

$$\pi = -\varphi + c\varphi_c \tag{5.19}$$

and $v_\alpha = \frac{w_\alpha}{\rho c}$, $\xi(c) = \frac{\Lambda(c)}{\rho(1-c)}$. We regard now $\pi(c)$ and $\xi(c)$ appearing in (5.18) as phenomenological parameters through which the individual features of solvent-polymer mixtures are expressed on the (c,**w**)-level. By using the standard terminology, their

characterization will be called a constitutive relation on (c,w)-level or simply a constitutive relation. Equations (5.18) together with Eqs.(5.17) and (5.8), allowing to calculate the polymer structure and the extra stress tensor from solutions of (5.18), constitute the governing equations of (c,w)-model.

We now proceed to investigate solutions to (5.18). We begin with three useful observations. First, we note that the set of equations (5.18) is the set of first order differential equations of the type

$$A^0(u)\partial_t u + A^\alpha(u)\partial_\alpha u = f(u) \tag{5.20}$$

Second, the nondissipative part of (5.18) (i.e. (5.18) in which we put ξ=0) is a set of local conservation laws, i.e. equations of the form

$$\partial_t F^0(u) + \partial_\gamma F^\gamma(u) = 0 \tag{5.21}$$

where the quantities A and F are related by $A^\alpha = \frac{\partial F^\alpha}{\partial u}$. Third, we observe that if we replace in (5.18) the solvent concentration c by the mass density ρ, the osmotic pressure π by the hydrostatic pressure p, and interpret v as the velocity of a fluid, then the nondissipative part of (5.18) becomes exactly the same as the nondissipative part (i.e. the Euler part) of the governing equations representing compressible simple fluids. These three observations will be very useful in the subsequent investigation of properties of solutions of (5.18).

From the third observation, we conclude that (5.18) represents a particular realization of GENERIC. This is because the nondissipative part of the governing equations of compressible simple fluids is known to be a particular realization of GENERIC. Indeed, we can easily verify by direct calculations that (5.18) is a particular realization of Eq.(4.27) in [See Chapitre 4 ou El Afif et al. (1999)] with the Poisson bracket

$\{A,B\}=\int dr[\chi_\gamma(\partial_\alpha(A_{\chi_\gamma})B_{\chi_\alpha}-\partial_\alpha(B_{\chi_\gamma})A_{\chi_\alpha})+c(\partial_\alpha(A_c)B_{\chi_\alpha}-\partial_\alpha(B_c)A_{\chi_\alpha})]$ and the dissipation bracket $[A,B]=\int dr A_{\chi_\alpha}\xi B_{\chi_\alpha}$, where $\chi=cv$, A and B are sufficiently regular functionals of c and χ. An important consequence of (5.18), being a particular realization of GENERIC, is that we automatically know an important property of solutions of (5.18). As $t\to\infty$, solutions to (5.18) approach the states that minimize the functional $\Phi(c,v)=\int dr(\frac{1}{2}cv^2+\frac{1}{\rho}\varphi(c))$. We recall that all the time evolution equations with which we have started our discussion in [El Afif et al. (1999)] are particular realizations of GENERIC. In order to arrive from these equations to (5.18), we have used however constraints (5.2), (5.3) and (5.6) and the approximations that led us from (5.7) to (5.18). The constraints and the approximations do not preserve, in general, GENERIC structure.

Now we shall derive some consequences of the first observation. Since many experimental observations of the solvent penetration are made in one dimensional settings, we shall also simplify our analysis by limiting ourselves to one spatial dimension. The one space coordinate will be denoted by the symbol x. Under this limitation, u, A, f and F in (5.20) and (5.21) become:

$$u=\begin{pmatrix}c\\v\end{pmatrix},\quad A^0=\begin{pmatrix}1&0\\v&c\end{pmatrix},\quad A^1=\begin{pmatrix}v&c\\v^2+\left(\pi_c/\rho\right)&2cv\end{pmatrix},$$

$$f(u)=\begin{pmatrix}0\\-\xi v\end{pmatrix},\quad F^0=\begin{pmatrix}c\\cv\end{pmatrix},\ \text{and}\ F^1=\begin{pmatrix}cv\\cv^2+\left(\pi/\rho\right)\end{pmatrix}. \tag{5.22}$$

Solutions to (5.20) and (5.21) have been extensively studied (see e.g. [Courant et al. (1942), Mueller et al. (1998)]). Below, we shall briefly recall results concerning the wave propagation and the formation and propagation of discontinuities (shock waves).

In the context of a compressible gas, the propagation of periodic disturbances in the mass density ρ and the gas velocity v are called sound waves. Following the established terminology according to which a pressure takes in the context of diffusion the name osmotic pressure, we suggest to call the propagation of periodic disturbances in the solvent concentration c and in the diffusion velocity v osmotic waves. Similarly as the

sound waves can be created by a mechanical vibration of a membrane, the osmotic waves can be, in principle, created by periodically changing the solvent penetration of a membrane separating the solvent and the solvent-polymer mixture. The standard discussion of the wave propagation associated with (5.19) proceeds as follows: We look for solutions of (5.18) in the form $u = u_{eq} + \tilde{u}\exp i(\omega t + kx)$, where $u_{eq} = (c_{eq},\ 0)^T$ is the unperturbed solution of (5.18). By inserting this u into (5.18) and keeping only the terms linear in $\tilde{u}$, we arrive at the dispersion relation k=k(ω).

If k designates the complex wave number $k=k_{re}+ik_{im}$ then the dispersion relation is

$$1 - \frac{i}{\omega}\xi - \kappa\left(\frac{k}{\omega}\right)^2 = 0 \tag{5.23}$$

where we have used $\kappa = \frac{1}{\rho}(\pi_c)_{|c=c_{eq}}$. Eq. (5.23) leads then to the following expressions for the phase velocity

$$v_{ph} = \frac{\omega}{k_{re}} = \sqrt{\frac{2\kappa}{1+\sqrt{1+\left(\frac{\xi}{\omega}\right)^2}}} \tag{5.24}$$

and for the intensity attenuation

$$\alpha(\omega) = -2k_{im}(\omega) = \frac{\xi v_{ph}}{\kappa}, \tag{5.25}$$

If $\omega \to \infty$, then we find that the phase velocity v_{ph} of the osmotic sound waves is:

$v_{ph} = \sqrt{\kappa} = \sqrt{\frac{\pi_c}{\rho}}$, (we assume that $\pi_c > 0$) and the attenuation is $\alpha = \frac{\xi}{\sqrt{\kappa}}$

For small frequencies i.e. $\omega \to 0$, the phase velocity is $v_{ph} \approx \sqrt{\frac{2\kappa\omega}{\xi}}$ and the attenuation becomes $\alpha(\omega) \approx \sqrt{\frac{2\xi\omega}{\kappa}}$. These low frequency expressions are the well-known results predicted by the classical Fick`s law.

Now, we proceed to discuss discontinuous solutions of (5.18). First, we identify the two characteristics associated with (5.18). Both characteristics are curves $\tau \mapsto (t(\tau), x(\tau))$ in the (x, t)-plane, τ denotes a parameter. The first one, denoted C_1, is generated by $\frac{dt}{d\tau} = 1, \frac{dx}{d\tau} = v - \sqrt{\frac{\pi_c}{\rho}}$ and the second one, denoted C_2, is generated by $\frac{dt}{d\tau} = 1, \frac{dx}{d\tau} = v + \sqrt{\frac{\pi_c}{\rho}}$. We can thus conclude that (5.19) is a time-hyperbolic system of equations if $\pi_c > 0$. Since (5.18) is also a nonlinear system of equations, the characteristics depend on (c, v) and can thus intersect. Intersections of characteristics are then an indication of a possible formation of a discontinuity in the solution. In order to be able to make some conclusions about discontinuous solutions of (5.18), we have to know how to interpret (5.18) if c(x, t) and v(x, t) become discontinuous. Here comes into use the form (5.21) of (5.18). The nondissipative part of (5.18) (i.e. the part of (5.18) obtained by putting $\xi = 0$; note that it is the only part of (5.18) that involves derivatives) represents conservation laws for c and cv (since the overall mass density ρ is constant). In the case of discontinuous solutions, we then naturally replace (5.18) by a "discontinuous version ", also called a weak version [Chorin et al. (1990)]:

$$-s[F^0] + [F^1] = 0 \tag{5.26}$$

where $[A] = A_{left} - A_{right}$, A_{right} is the assigned unperturbed value of the quantity A in front of the shock, A_{left} is the value of the quantity A behind the discontinuity, and s is

the velocity of the discontinuity (shock, etc.). Equations (5.26), called Rankine-Hugoniot equation, are two equations for three unknown s, c_{left}, v_{left}. Let solutions to (5.26) be

$$c_{left} = c_{left}(c_{right}, v_{right}, \varsigma), v_{left} = v_{left}(c_{right}, v_{right}, \varsigma), s = s(c_{right}, v_{right}, \varsigma),$$

where ς is a parameter. Nontrivial solutions bifurcate from the trivial solution $c_{left} = c_{right}$, $v_{left} = v_{right}$, $s = v_{right} \pm \sqrt{\left.\frac{\pi_c}{\rho}\right|_{c_{right}}}$. If we take the coordinate system that moves with the discontinuity, i.e. we introduce a new velocity v^* by $v^* = v - s$, then Eqs. (5.26) become

$$c_{left} v^*_{left} = c_{right} v^*_{right}$$

$$\rho c_{left}(v^*_{left})^2 + \pi_{left} = \rho c_{right}(v^*_{right})^2 + \pi_{right} \tag{5.27}$$

that then imply

$$(c_{left} v^*_{left})^2 = (c_{right} v^*_{right})^2 = -\frac{\pi_{left} - \pi_{right}}{\rho\left(\frac{1}{c_{left}} - \frac{1}{c_{right}}\right)},$$

$$v^*_{left} v^*_{right} = \frac{\pi_{left} - \pi_{right}}{\rho(c_{left} - c_{right})} \tag{5.28}.$$

It is interesting to note that the jump in the mass density of the solvent, has also been investigated, but in the context of classical Case II model, in [Edwards (1995), Edwards et al. (1995)]. In that context, this jump arises as a consequence of the choice of the model parameters (i.e. the choice of constitutive relations on (c,m)-level). These relations are chosen to involve jumps in the dependence on c. From the physical point of view, this means that a transition of the glass-rubber type is imposed at the outset of the investigation. The jump in the mass density of the solvent is called in [Edwards (1995),

Edwards et al (1995)] a 'phase change' parameter. We see in (5.26) that, in the context of (c,w)-model, we do not need to impose the glass-rubber transition in constitutive relations to see a jump in the mass density of the solvent in solutions of the governing equations. Moreover, we relate the jump in the mass density to the jump in the diffusion flux, $\rho[c]=\frac{[w]}{s}$. Of course, the glass-rubber transitions can also be investigated in the context of (c,w)-model. Because of the analogy between (5.18) and the governing equations of classical hydrodynamics of compressible simple fluids, such investigation will be analogical to investigations of the wave propagation and formation of discontinuities in van der Waals fluids undergoing gas-liquid phase transitions [Slemrod (1983)].

The similarity of the governing equations (5.19) of (c,w)-model and the governing equations of compressible simple fluids suggests also the following terminology. We introduce a dimensionless parameter

$$M_{diff}=\frac{v}{\sqrt{\kappa}} \tag{5.29}$$

that we shall call a diffusion Mach number. The diffusion will be called super-osmotic if $M_{diff}>1$, sub-osmotic if $M_{diff}<1$, and osmotic if $M_{diff}=1$.

Before leaving the discussion of discontinuous solutions of (5.18), a word of caution is in order. We recall that Eqs. (5.7) as well as Eqs.(5.18) have been derived under the assumption of constant temperature. It is well known that the propagation of shock waves in compressible simple fluids involves local nonisothermal processes. It is possible that a stronger coupling between the large scale motion of the macromolecules (taken into account in the conformation tensor **m**) and the small scale motion of atoms composing the macromolecules (taken into account in the temperature) develops, in the location of discontinuities, also during Case II diffusion. To the best of our knowledge, such coupling has not been however observed. On the contrary, two observations, namely the fact that on both sides of the singularity the polymer remains in glassy state and another fact that there is no change in temperature before and after the penetration,

indicate clearly that nonisothermal effects do not play an important role in Case II diffusion.

If we want to obtain a more detailed information about solutions to (5.18), we have to turn to numerical solutions. We shall rewrite (5.18) into the form:

$$\frac{\partial c}{\partial t} = -\partial_\gamma (c v_\gamma)$$

$$\frac{\partial v_\gamma}{\partial t} = -v_\alpha \partial_\alpha v_\gamma - \frac{\xi(c)}{c}\left(v_\gamma + D\partial_\gamma \ln c\right) \qquad (5.30)$$

where $D(c)=\frac{c\pi_c}{\rho\xi}$ is the diffusion coefficient. For the later use we shall introduce $D_0:=D(0)$. As in the analysis of the osmotic wave propagation, we will limit ourselves to the one dimensional diffusion. The one-dimensional description is particularly appropriate for investigating penetration of small molecules into thin polymeric materials. The system under consideration is a system consisting of a solvent composed of small molecules and a thin film of glassy polymer of thickness $2L_o$. The polymer is initially dry, so that the state variables (c, w) initially equal to zero within the whole polymer film excluding the boundaries. At the both polymer-solvent interfaces, the concentration attains an equilibrium concentration c_{eq}. This value is reached more or less rapidly depending on the value of the relaxation time ($\propto \xi^{-1}$). The evolution of the surface concentration will be investigated in Part II of this series of papers. In this paper, we focus our attention on the stage in which the interface concentration has already reached its equilibrium value c_{eq}. On the same footing, we assume that the penetration velocity of the solvent into the polymer has initially a prescribed value v_{in}. In order to transform (5.30) into the dimensionless form, we introduce the following quantities:

$$X=\frac{x}{L_o},\quad \theta=\frac{tD_o}{L_o^2},\quad V=\frac{v}{v_{in}},\quad C=\frac{c}{c_{eq}} \tag{5.31}$$

where D_0:=D(0). The governing equations (5.30) become

$$\frac{\partial C}{\partial \theta}=-\frac{\partial (CV)}{\partial X}$$
$$\frac{\partial V}{\partial \theta}=-V\frac{\partial V}{\partial X}-\frac{1}{De(C)}\left(V+\tilde{D}(C)\frac{\partial \ln C}{\partial X}\right) \tag{5.32}$$

These equations involve two functions De and $\tilde{D}$ of C. The first one, De(C), called a w-Deborah number, is defined by

$$De(C)=\frac{D_0(1-c_{eq}C)^2}{L_0^2\tilde{\xi}} \tag{5.33}$$

where $\frac{\tilde{\xi}(c)}{(1-c)^2}=\frac{\xi(c)}{c}$ is the inverse of the relaxation time. The second is the dimensionless diffusion coefficient $\tilde{D}(C)=\frac{D(C)}{D_0}$, where D_0=D(0). It is in these functions where the individual features of the system under consideration are expressed in the governing equations (5.32) of the (c,w)-model. In order to continue, we have to specify these functions. In other words, we have to now specify the constitutive relations on the (c,w)-level. In the context of (c,w,m)-model, that we shall discuss in detail in Part II, the parameters through which the individual features are expressed have clearer physical meaning (e.g. one of the parameter is the free energy) so that it is easier to use our physical insight to specify them. In the context of (c,w)-model, the specification has to be completely phenomenological. We recall that in (c,w)-model as well as in the c-model

(see Section 5.5.1) where the state variable m characterizing the polymer structure is absent, it is in the phenomenological dependence on the solvent concentration of the parameters entering the models where we express implicitly the changes of the polymer structure accompanying the diffusion. Following [Thomas et al. (1982), Fu et al. (1993), Wu et al. (1993)], we shall assume that both the diffusion coefficient D and $\tilde{\xi}$ increase exponentially with the solvent concentration, i.e.

$$\tilde{D}(C) = \frac{D(C)}{D_0} = e^{kC} \quad \text{and} \quad \tilde{\xi} = \tilde{\xi}_0 e^{rC}, \tag{5.34}$$

where k and r are considered to be material constants. Using the diffusion Mach number $M_{diff,0}$ at the initial state and the fact that $\kappa_0 = \tilde{\xi}_0 D_0$ we obtain

$$\begin{aligned} De(C) = \frac{D_0(1-c_{eq}C)^2}{\tilde{\xi}(c)L_0^2} &= \left(\frac{D_0(1-c_{eq}C)}{\sqrt{\kappa_0}L_0}\right)^2 e^{-rC} \\ &= \left(\frac{D_0 M_{diff,0}(1-c_{eq}C)}{v_0 L_0}\right)^2 e^{-rC} \end{aligned} \tag{5.35}$$

This represent a one-to-one relation between two dimensional numbers, De and M_{diff}. We shall use often M_{diff} instead of De. Assuming that the front velocity for Case II diffusion is approximately of the same order as D_0/L_0 (since the velocity is constant during the whole process of Case II diffusion), the relation (5.35) can be simplified. We arrive at a simple expression

$$De(C) \approx \left(M_{diff,0}(1-c_{eq}C)\right)^2 e^{-rC} \tag{5.36}$$

It is $M_{diff,0}$ that has to be appropriately chosen to recover the different types of diffusion.

Now, we turn our attention to the initial and boundary conditions. We shall specify them as follows:

$$\begin{aligned} C(X,0) &= 0 \\ V(X,0) &= 0 \\ C(0,\theta) &= 1 \\ V(0,0) &= 1 \end{aligned} \tag{5.37}$$

From (5.32) and the third equation in (5.37), we deduce that the decay of the velocity at the interface is governed by

$$\left.\frac{\partial V}{\partial \theta}\right|_{X=0} = -\frac{V(0,\theta)}{De(C)} \tag{5.38}$$

This equation can be solved either analytically or numerically provided the initial condition for the interface is known. If we consider the fourth equation in (5.37) to be such initial condition, the analytical solution of (5.38) is:

$$V(0,\theta) = e^{-\frac{\theta}{De(1)}} \tag{5.39}$$

Everything has been now specified and we can thus proceed to numerical solutions of (5.32). We begin to illustrate implications of (c,w)-model on the example in which the polymer does not undergo the glass-rubber transition. For example, we have in mind the observations, reported in [Thomas et al. (1978, 1981), Barriere (1997)], of diffusion in glassy polymers characterized by a very large glass temperature relative to the temperature at which the observations are made. In that case, the phenomenological parameters D and De can be regarded as constants independent of the concentration. We thus put k=0, r=0 in (5.34). Note that even under this assumption, the solvent front velocity and the mass flux equations remain still highly nonlinear equations. The

parameters used in the calculations are those corresponding to the methanol-poly(methyl methacrylate) near room temperature (see Table 5.1).

The solvent concentration profiles for $M_{diff,0}$ =7 (the lines drawn in dots) and for $M_{diff,0}$=100 (the continuous lines), are shown in Figure 5.1. The profiles are sharp; moreover, one notices the absence of the concentration gradients behind the moving front particularly for $M_{diff,0}$=100. This is in conformity with the familiar experimental observations reported for Case-II diffusion. Similarly, the velocity profiles are almost step-like for $M_{diff,0}$=7 and are sharper for $M_{diff,0}$=100 (Figure 5.2). The normalized mass-uptake (Figure 5.3) curves are presented for $M_{diff,0}$=1, 3, 5, 7, 9, 15, 20 and 50. For $M_{diff,0}$ greater than 5, the mass uptake follows a linear kinetics. For $M_{diff,0}$=7, the total time for a complete penetration is closer to the value reported in [Thomas et al. (1978)]. However, there is no induction time at small diffusion times. This is probably due to the fact that we started the simulation assuming that the interface reaches instantaneously its equilibrium value. In Part II, in the context of (c,w,m)-model, we predict the induction time.

In Figures 5.4, 5.5 and 5.6, we present the profiles of the solvent concentration, velocity, and the mass-uptake respectively that are typical of thicker polymer films showing a deviation from Case II diffusion. This has been observed for methanol-PPMA if the thickness of the film is increased three times [Thomas et al. (1978)]. It becomes clear from Eq.(5.35), that the Deborah number has to be decreased by 9. The parameters involved in the model are chosen to be: $M_{diff,0}$ =9, k = 0, r = 5. We have remarked that the stronger is the dependence of the relaxation time on the concentration, i.e. the larger is r, the more pronounced are the gradients of concentration behind the front and also the values of the induction time. We thus see that the constitutive equations influence significantly the shape of the computed profiles. They must be chosen therefore very carefully to fit as accurately as possible the measured data. Our calculations show that the velocity profiles and stresses tensor become more sensitively dependent on the constitutive relations than in the case where D and De are chosen to be constants. The most sensitive dependence appears in particular in the neighborhood of the front where

the material is separated into two different regions, rubbery and glassy, that have different mechanical responses.

To recover the classical Fickean description, the w-Deborah number must be very small (this means that the reaction of the polymeric chains to diffusion is instantaneous). We simulate this case by choosing $M_{diff,0}$ =0.001, k = 0 and r = 0. The profiles calculated with these constitutive relation (that represent classical Fickean medium in (c,w)-model) are shown in Figures 5.7, 5.8 and 5.9. It is worth to mention that, following the introduced terminology, Fickian diffusion can be regarded simply as a sub-osmotic diffusion, while Case II diffusion is a super-osmotic diffusion.

Summing up, (c,w)-model developed in this section is both relatively simple from the mathematical point of view and relatively faithful to the physics of Case II diffusion. Its mathematical simplicity is manifested by the similarity of its governing equations with the governing equations of compressible simple fluids. All mathematical results developed for these well studied equations can be now used in the context of the nonstandard diffusion. The faithfulness of (c,w)-model to the reality is manifested by displaying, in solutions of its governing equations, all the most important features of the observed Case II diffusion even in the case where no glass-rubber transition accompanies the diffusion. We have also shown that solutions of the governing equations of the (c,w)-model represent Case I diffusion (the Fickian diffusion) for small w- Deborah numbers De. The disadvantage of (c,w)-model is its phenomenological nature in the sense that the model does not involve explicitly, as an independent state variable, the polymeric structure and consequently it needs to be supplemented by phenomenological constitutive relations (specification of the diffusion coefficient and of the relaxation time as functions of the solvent concentration). We emphasize that the polymeric structure as well as the extra stress tensor remain still in the model as dependent state variables. Equations (5.8) and (5.17) are formulas expressing the conformation tensor and the extra stress tensor in terms of solutions of (5.18). In Part II of this series of papers we shall return to (c,w,m)-model represented by Eqs.(5.7). We shall demonstrate that while Eqs.(5.7) are

considerably more flexible and easier to apply to specific situations than Eqs. (5.18), they are not much more difficult to solve than Eqs.(5.18).

Table 5.1: parameters, typical of methanol-PMMA, used for the case II simulation

Half thickness, L_o	[m]	$0.5\ 10^{-3}$
c_{eq}		0.21
v_{in}	[m/s]	$1.8\ 10^{-9}$
Diffusion Coefficient, D_o	[m^2/s]	$0.9\ 10^{-12}$
Diffusion Mach number, $M_{diff,o}$		7
Temperature, T	[Kelvin]	297
(k, r)		(0, 0) no phase transition

5.7. Conclusion

The main result of this paper is the set of the governing equations (Eqs.(5.7)) of a new model of isothermal diffusion of a solvent into a polymer under the condition of the overall mechanical equilibrium. We call the model a (c,w,m)-model since the solvent concentration c, the diffusion flux w, and the conformation tensor m play in it the role of independent state variables. After deriving the model, we have compared it with other models of classical and non-classical diffusion. In Part II of this series we then further investigate solutions to (5.7) and compare them with results of experimental observations reported in the literature.

The information that we have collected about solutions to (5.7) in this paper can be summarized as follows. First, we have noted that (5.7) is a system of first order partial differential equations. This then means that the large body of results obtained for these

equations can be immediately used in the context of diffusion. Second, we have shown that by choosing appropriately the parameters entering (5.7) we arrive at simpler models in which some of the state variables become dependent state variables. For example, when we derive from (5.7) the classical Fickian diffusion equation, i.e. a theoretical description of diffusion in which the only independent state variable is the solvent concentration c), we also derive formulas expressing $\mathbf{w}$, $\mathbf{m}$, and σ, that become dependent state variables, in terms of c. Beside the Fickian model, we have identified among the models that arise as approximations of (c,w,m)-model also the classical as well as the extended [Mavrantzas et al. (1992), Beris et al. (1994)] Case II models, and, in addition, one new mode. We call the new model a (c,w)-model since the solvent concentration c and the diffusion flux $\mathbf{w}$ play in it the role of independent state variables. For the remaining variables, namely $\mathbf{m}$ and the extra stress tensor σ, the derivation provides formulas allowing to calculate them in terms of c and $\mathbf{w}$.

(c,w)-model and the classical Fickian model have many common features and they are also complementary. What they have in common is that they are both relatively very simple from the mathematical point of view, they are both phenomenological, and they have both a limited domain of applicability. They are complementary since their domains of applicability are complementary. By the mathematical simplicity, we mean that mathematical aspects of their governing equations have been extensively investigated and a lot is known about their solutions. This is, of course, true for the classical diffusion equation, but it is also true for the governing equations of (c,w)-model since its governing equations are very similar to the governing equations of compressible simple fluids. This similarity allowed us, for example, to adapt the well known analysis of the propagation of discontinuities in simple compressible fluids to the propagation of discontinuities in diffusion. A model is said to be phenomenological if it requires, as a part of its input, a specification of the parameters entering it as phenomenological functions of the independent state variables. In the classical diffusion equation, it is the specification of the diffusion coefficient as a function of the solvent concentration c. In (c,w)-model it is the specification of two parameters (the diffusion coefficient and the relaxation time of

w) as a function of the solvent concentration. Of course, according to this definition, all macroscopic models are phenomenological. However, the more microscopic is the model (for example, (c,w,m)-model is more microscopic than (c,w)-model) the easier it is to see the physics in the parameters entering it and consequently the less phenomenological is their specification. The domains of applicability of the Fickian diffusion and (c,w)-model are centered in the classical Case I diffusion and Case II diffusion respectively. We have shown that (c,w)-model reproduces successfully a wide range of experimental data that include for instance Case II diffusion observed in glassy polymers that do or do not undergo the glass-rubber transition.

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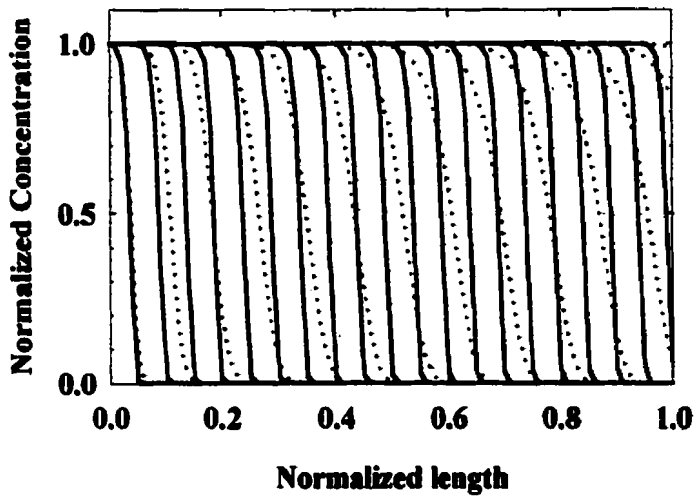

Figure 5.1 Normalized concentration versus normalized length calculated for k=0, r=0 and for M_{diff}=7 (...) and M_{diff}=100 (—) respectively. The profiles are shown every 0.1 normalized time step.

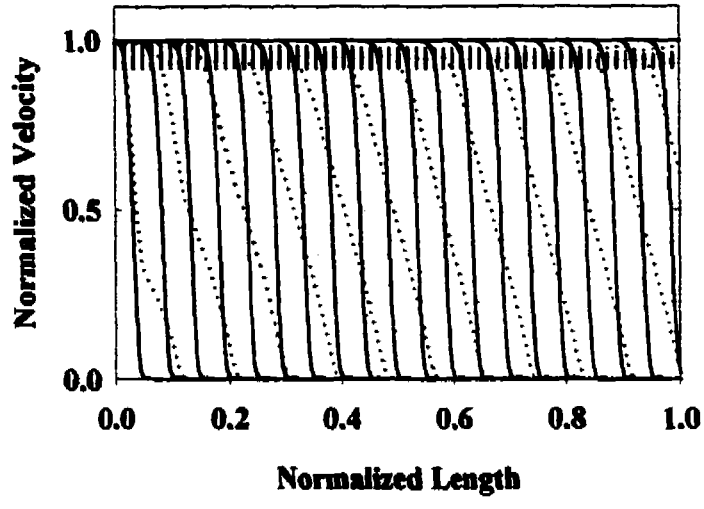

Figure 5.2 Normalized velocity versus normalized length calculated for k=0, r=0 and for M_{diff}=7 (...) and M_{diff}=100 (—) respectively. The profiles are shown every 0.1 normalized time step

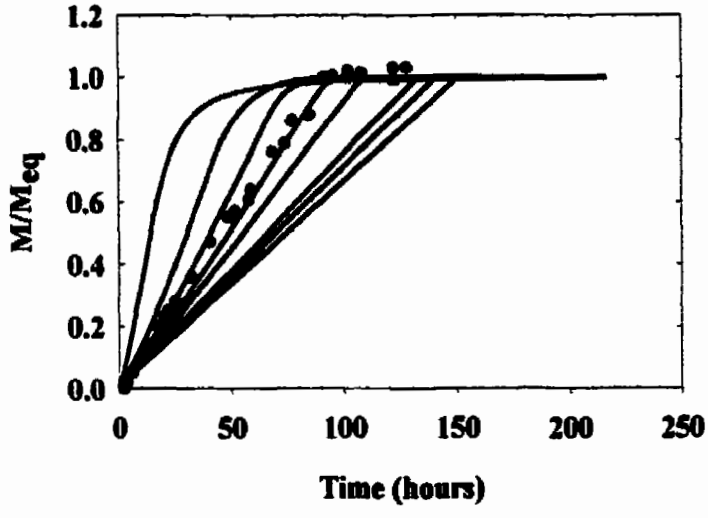

Figure 5.3 Normalized weight gain versus time (in hours) calculated for the parameters k=0, r=0. The curves are shown, from left to right, for the following values of $M_{diff,0}$ = 1, 3, 5, 7, 9, 15, 20 and 50. The curve in (•) represents the experimental data for methanol-PMMA mixture [Thomas et al. (1978)].

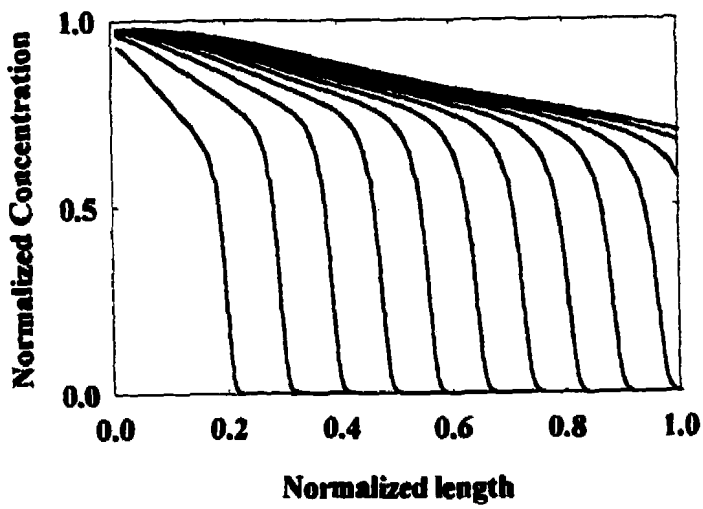

Figure 5.4 Normalized concentration versus normalized length calculated for $M_{diff,0}$=9 k=0, r=5. The profiles are shown every 0.0045 normalized time step.

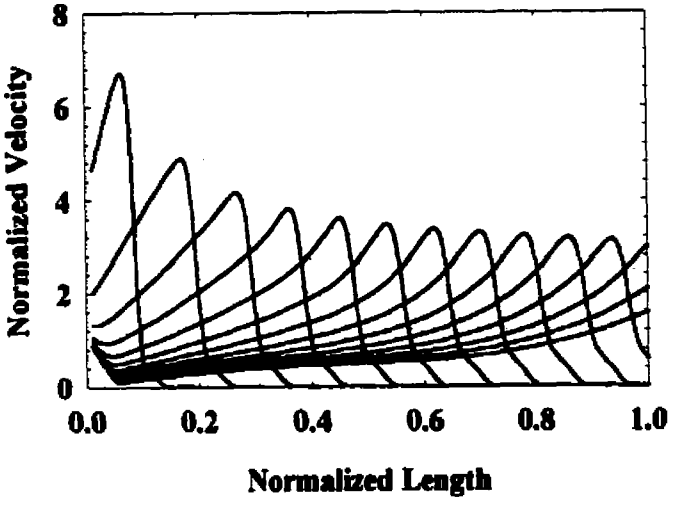

Figure 5.5 Normalized velocity versus normalized length calculated for $M_{det,0}$=9 k=0, r=5. The profiles are shown every 0.0045 normalized time step.

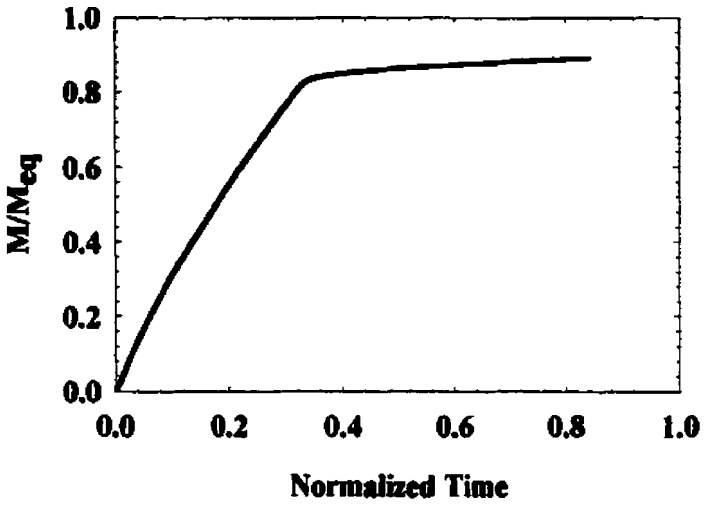

Figure 5.6 Normalized weight gain versus normalized time calculated for $M_{diff,0}$=9 k=0, r=5.

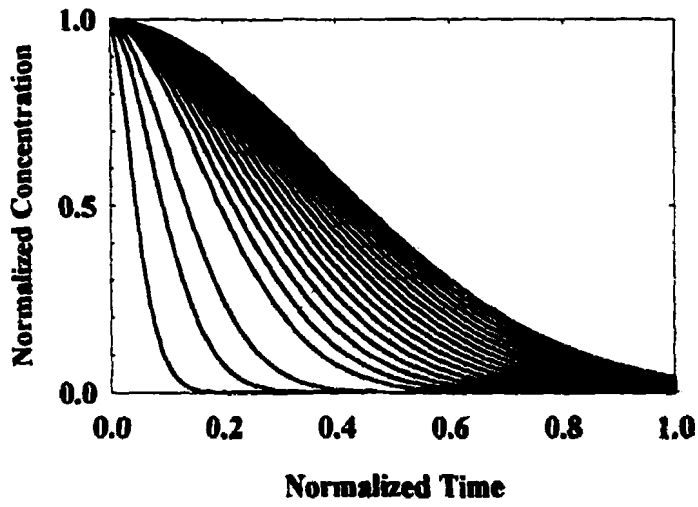

Figure 5.7 Normalized concentration profiles versus normalized length calculated for $M_{diff,0}$=0.001, k=0, r=0. The profiles are shown every 0.004 normalized time step.

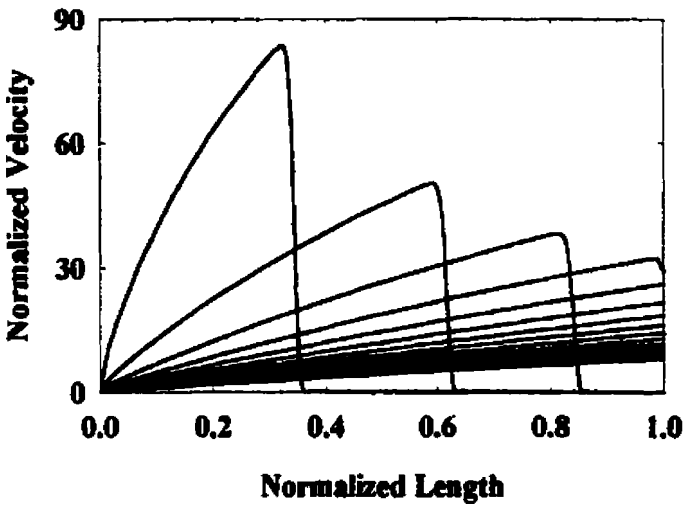

Figure 5.8 Normalized velocity profiles versus normalized length calculated for $M_{diff,0}$=0.001, k=0, r=0. The profiles are shown every 0.004 normalized time step.

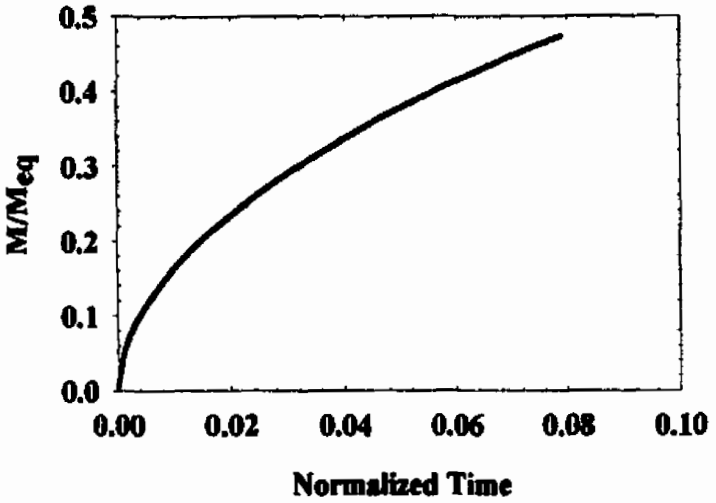

Figure 5.9 Normalized weight gain versus normalized time calculated for $M_{diff,0}$=0.001, k=0, r=0.

CHAPITRE 6

NON-FICKIAN MASS TRANSPORT IN POLYMERS. II

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6.1. Abstract

The new model of isothermal diffusion in a polymeric medium in the absence of an overall flow and in mechanical equilibrium, that was introduced in Part I, is investigated in its entirety. First, we derive its implication for the wave propagation of disturbances in the solvent concentration. Next, we specify the free energy appearing in the general governing equations (we choose the free energies corresponding to the Maxwell and the FENEP rheological models) and then solve the governing equations. In spite of the fact that the number of equations is larger than in classical models, we demonstrate that it is easier to find (both analytically and numerically) properties of their solutions. By solving the governing equations, we obtain the time evolution of the solvent concentration, the diffusion flux, the swelling, the internal deformations and stresses, and the internal viscosity associated with the solvent penetration and the swelling. The governing equations involve three parameters: relaxation time of the polymeric structure, relaxation time of the diffusion flux, and one parameter expressing the coupling of the polymeric structure and the solvent concentration in the free energy. As an illustration, we show that with an appropriate choice of these three parameters we reproduce results of several observations that we have selected from the literature [N. L. Thomas and A. H. Windle, Polymer, 19, 255 (1978)]. In particular, we reproduce the observed Case II type diffusion in the absence of the glass-rubber transition

6.2. Introduction

Our aim is to study the process of diffusion of a solvent into a dry polymer on macroscopic and mesoscopic levels of description. The governing equations are derived in two stages. In the first stage, the focus is put on the comparison of their solutions with the observed compatibility with equilibrium thermodynamics (externally unforced systems are seen to approach equilibrium states at which their behavior is found to be well described by equilibrium thermodynamics). The requirement of the agreement with this type of observations leads to an overall structure of the governing equations. The structure is then filled out, or in other words, particular realizations of the structure is searched, in the second stage. The microscopic model of diffusion that is used to guide the second stage is the following. The system under consideration is composed of two types of molecules: relatively small solvent molecules and larger and more complex polymer molecules. Initially, the solvent and the medium are separated, the diffusion begins when the separation is removed. In the absence of external forces, the molecules of the solvent experience the thermal motion. It is this type of motion that carries them into the medium. How does the medium react to their presence? Let us consider three possibilities. First, the medium is accepting them passively or, if some rearrangements in the medium are needed, they take place very rapidly so that the solvent molecules do not even notice them. On the macroscopic level, this diffusion process presents itself as the so called classical Fickian diffusion (also called a Case I diffusion). The second possibility is that in order to accommodate the solvent, the medium has to be continuously rearranged. Since the medium is a global network of tightly nit polymer molecules, the rearrangements have to be global in their nature and as such they are slow. The molecules entering the medium have to in fact wait for the appropriate rearrangements to take place. On the macroscopic level, this diffusion process presents itself as the so called Case II diffusion [Alfrey et al. (1966), Thomas et al. (1978)]. The

third type of interaction of the solvent and the medium is a combination of the first two. The resulting macroscopic diffusion process is then called an anomalous diffusion.

The macroscopic description of Case I diffusion is well known. The only independent state variable is the field of the solvent concentration c(r,t), r denotes the position vector, t is the time. The time evolution of c(r,t) is governed by the classical diffusion equation. The individual features of the system under consideration are expressed in this equation only in one parameter, namely in the diffusion coefficient D. Specification of D as a function of c will be called a constitutive relation on the level of the Fickian theory.

The macroscopic description of Case II diffusion is, of course, more complex. This is because the rearrangements that take place in the medium during the diffusion process are expected to depend very sensibly on the specific nature of the polymeric medium. The aim of this series of two papers is to introduce a macroscopic description of diffusion (including Case I, Case II and anomalous diffusion processes) that is both realistic and simple from the mathematical point of view. A model with these attributes has been derived in Part I (its governing equations are Eqs. (5.7)) where it has also been shown that many theoretical descriptions of diffusion introduced previously (for example classical Case II models [Thomas et al. (1982), Durning et al. (1986), Wu et al. (1993)]) are its approximations. In this Part II of the series, we continue to discuss solutions of the governing equations of the new model (Eqs.(5.7)). We shall also compare them with some experimental observations reported in the literature.

From the results of Part I, we recall how does the new model improve the classical Case II models [Thomas et al (1982), Durning et al. (1986), Wu et al. (1993)] in which the medium is represented by the field of the extra stress tensor σ(r,t). The classical models have the following disadvantages: (i) Their governing equations are rather complex from the mathematical point of view. This is mainly because they do not fall into any of the traditionally well studied classes of partial differential equations. Although some interesting results of the mathematical nature for the governing equations

of the classical Case II models have recently appeared [Edwards et al. (1995)], the results are still much less powerful and less complete than the results known for the standard classes of the partial differential equations [Godlewski et al. (1991), Smoller (1983)]. (ii) Rheology of the medium into which the solvent penetrates is oversimplified. This disadvantage is however removed in extended Case II models that have been introduced in [Mavrantzas et al. (1992), Beris et al. (1994)] and that also arise in Part I as approximations of the new model. (iii) The classical as well as the extended Case II models do not seem to predict shock wave-type propagation of the solvent observed experimentally [Alfrey et al. (1966), Thomas et al. (1978), Barriere (1997)] in a medium that does not experience during the diffusion process the glass-rubber transition. The new model (we call it a (c,w,m)-model since the independent state variables in it are the field of the solvent concentration c(r,t), the field of the diffusion flux w(r,t), and the field of the conformation tensor m(r,t)) is simpler from the mathematical point of view (its governing equations fall into a class of well studied partial differential equations), it is very flexible in expressing rheology of the medium, and it does predict the formation of discontinuities in both the presence and the absence of glass-rubber transitions.

This Part II of the series is organized as follows. We begin (Section 6.3) by a brief discussion of the propagation of waves predicted by Eqs.(5.7). In Section 6.4, we transform Eqs.(5.7) into a new form that is suitable for further analytical and numerical study of its solutions. In particular, we pass to material coordinates in order to be able to calculate the swelling of the polymeric medium. In Section 6.5, we commit ourselves, for the first time, to a specific free energy. For the sake of simplicity, we choose only two free energies: the Maxwell free energy (the polymer molecules of the medium are seen as Hookean dumbbells) and the FENEP free energy (the polymer molecules of the medium are seen as finitely extensible Hookean dumbbells). Both free energies are appropriately modified to take into account the swelling. Finally, in Section 6.6, we present numerical solutions and compare them with results of some experimental observations reported in the literature [Thomas et al. (1978)].

6.3. Traveling Waves

Our starting point are Eqs.(5.7) derived in Part I. These equations describe the time evolution of (c, w, m). In Part I, we have tried to simplify them before discussing their solutions. In this paper, we shall solve them directly. Our aim is to demonstrate that (5.7) represents a single model that is both relatively simple and faithful to the reality. We begin our discussion of solutions of (5.7) by noting that this system of equations can be cast into the form

$$A^0(u)\partial_t u + A^\alpha(u)\partial_\alpha u = f(u) \tag{6.1}$$

If we restrict ourselves to one dimension (the one space coordinate is denoted by the symbol x) then

$$u=\begin{pmatrix} c \\ v \\ m \end{pmatrix},\ A^0=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},\ f=\begin{pmatrix} 0 \\ -\xi v \\ -\zeta m \end{pmatrix},\ A^1=\begin{pmatrix} v & c & 0 \\ \frac{1}{\rho}\varphi_{cc} & v & \frac{1}{\rho}\varphi_{cm} \\ \frac{vm}{(1-c)^2} & \frac{cm}{1-c} & -\frac{cv}{1-c} \end{pmatrix} \tag{6.2}$$

$v=\frac{w}{\rho c}$, $\zeta = 2\lambda\varphi_m\big|_{u_{eq}}$, $\xi = \frac{\Lambda}{\rho(1-c)}\Big|_{u_{eq}}$, φ is the density of the part of the free energy that is independent of v (see (5.5), ρ is the overall mass density (assumed to be a constant), $\varphi_{cc}(x)=\frac{\partial^2\varphi}{\partial c(x)\partial c(x)}$, similarly $\varphi_{cm}(x)=\frac{\partial^2\varphi}{\partial c(x)\partial m(x)}$; λ and Λ are two phenomenological parameters introduced in (5.7) (Λ is directly related to the inverse of the relaxation time of the diffusion flux w, λ is directly related to the relaxation time of the conformation tensor m) .

The three characteristics C_1, C_2, C_3 corresponding to (6.1), (6.2) are curves $\tau\to(t(\tau),x(\tau))$ in the (x,t) plane, τ is a parameter; C_1 is generated by $\frac{dt}{d\tau}=1,\frac{dx}{d\tau}=-\frac{cv}{1-c}$; C_2 is generated by $\frac{dt}{d\tau}=1,\frac{dx}{d\tau}=v-\sqrt{\frac{1}{\rho}(c\varphi_{cc}+\frac{cm}{1-c}\varphi_{cm})}$; C_3 is generated by $\frac{dt}{d\tau}=1,\frac{dx}{d\tau}=v+\sqrt{\frac{1}{\rho}(c\varphi_{cc}+\frac{cm}{1-c}\varphi_{cm})}$. We see thus that (6.1), (6.2) is a time-hyperbolic system of partial differential equations if $c\varphi_{cc}+\frac{cm}{1-c}\varphi_{cm}>0$.

The standard analysis (recalled in Part I) of the linear osmotic wave propagation (linearized about $u_{eq}=(c_{eq},0,m_{eq})^T$) leads to the following dispersion relation

$$-\left(\frac{k}{\omega}\right)^2\left(\kappa-i\frac{\zeta}{\rho\omega}c\varphi_{cc}|_{u_{eq}}\right)+\left(1-i\frac{\xi}{\omega}\right)\left(1-i\frac{\zeta}{\omega}\right)=0 \tag{6.3}$$

where $\kappa:=\frac{1}{\rho}\left(c\varphi_{cc}+\frac{cm}{1-c}\varphi_{cm}\right)\Big|_{u_{eq}}$. Introducing the complex wave number $k=k_{re}+ik_{im}$, we arrive at the following expression for the phase velocity

$$v_{ph}=\frac{\omega}{k_{re}}=\sqrt{\frac{2\kappa}{\sqrt{\left(1-\frac{2c_{eq}\varphi_{cc}(u_{eq})\zeta H(\omega)}{\rho\omega^3}-\frac{\xi\zeta}{\omega^2}\right)+\sqrt{\left(1-\frac{2c_{eq}\varphi_{cc}(u_{eq})\zeta H(\omega)}{\rho\omega^3}-\frac{\xi\zeta}{\omega^2}\right)^2+\frac{4H(\omega)^2\kappa^2}{\omega^4}}}}} \tag{6.4}$$

where

$$H(\omega)=-\frac{\omega\xi\zeta^2\rho c_{eq}\varphi_{cc}(u_{eq})+\left(\rho^2(\xi+\zeta)\kappa-\zeta\rho c_{eq}\varphi_{cc}(u_{eq})\right)\omega^3}{2\left(\rho^2\omega^2\kappa^2+\left(\zeta c_{eq}\varphi_{cc}(u_{eq})\right)^2\right)} \tag{6.5}$$

The attenuation α defined by $\alpha(\omega) = -2\,\mathrm{Im}(k) = -2k_{im}(\omega)$ is given by

$$\alpha(\omega) = \frac{\left(\xi\zeta^2\rho c_{eq}\varphi_{cc}(u_{eq}) + \left(\rho^2(\xi+\zeta)\kappa - \zeta\rho c_{eq}\varphi_{cc}(u_{eq})\right)\omega^2\right)v_{ph}}{\left(\rho^2\omega^2\kappa^2 + \left(\zeta c_{eq}\varphi_{cc}(u_{eq})\right)^2\right)} \tag{6.6}$$

In the limit $\omega\to\infty$, the phase velocity v_{ph} and the attenuation α become

$$v_{ph} = \sqrt{\kappa} \tag{6.7}$$

$$\alpha(\omega) = \frac{\left(\left(\rho(\xi+\zeta)\kappa - \zeta c_{eq}\varphi_{cc}(u_{eq})\right)\right)}{\rho\kappa\sqrt{\kappa}}.$$

For small frequencies $\omega\to 0$, the function H becomes $H(\omega) = -\dfrac{\rho\omega\xi}{2c_{eq}\varphi_{cc}(u_{eq})}$.

Consequently, the phase velocity and the attenuation are given by

$$v_{ph} = \frac{\omega}{k_{re}} \approx \sqrt{\frac{2\omega c_{eq}\varphi_{cc}(u_{eq})}{\rho\xi}}$$

$$\alpha(\omega) = \sqrt{\frac{2\omega\xi\rho}{c_{eq}\varphi_{cc}(u_{eq})}} \tag{6.8}$$

We see clearly that the results about the osmotic wave propagation obtained above reduce (by putting $\varphi_{em}=0$ and $\zeta=0$) to the results obtained in Part I for (c,w)-model (see Eqs.(5.24)-(5.26)).

Next, we would like to say something about possible discontinuous solutions to (5.1),(5.2). We note that Eqs.(6.1),(6.2) do not represent a set of local conservation laws (they cannot be cast into the form (5.22)). This then means that we cannot investigate their possible discontinuous solutions by using the standard methods [Smoller (1983),

Chorin et al. (1990), Godlewski et al. (1991), Dafermos (2000)] that we used in Part I in the context of (c,w)-model. At this point, we can say only that Eqs.(6.1) and (6.2) are nonlinear time-hyperbolic partial differential equations, their characteristics C_1,C_2,C_3 can thus intersect, and consequently, discontinuities in their solutions can develop. Numerical solutions discussed in Section 6.6 will provide further information.

6.4. Material Coordinates and Dimensionless Formulation

The rearrangements in the polymer film that are needed to accommodate the solvent cause the film to deform. This deformation, called a swelling, is often associated with a change of the volume of the film and thus also with a change of its boundaries. This then makes it difficult to formulate appropriately the boundary conditions. To overcome this difficulty, we shall follow [Wu et al. (1993)] and reformulate the governing equations of the diffusion in the material (also called Lagrangian) coordinates. The material coordinates will be denoted by the symbol $\mathbf{Y}$. We recall that the spatial (also called Eulerian) coordinates are denoted in this paper by $\mathbf{r}$. By applying the one-to-one transformation $\mathbf{r}\mapsto\mathbf{Y}$ to Eq. (5.7) we obtain

$$
\begin{aligned}
\rho\frac{\partial c}{\partial t} &= -F^{-1}_{v\alpha}\nabla_v w_\alpha \\
\frac{\partial w_\alpha}{\partial t} &= -F^{-1}_{v\beta}\nabla_v\left(w_\alpha v_\beta\right) - \frac{\tilde{\xi}(c)}{(1-c)^2}\left(w_\alpha + \rho D\, F^{-1}_{v\alpha}\left(\nabla_v c + L_{\rho\gamma}(c,\mathbf{m})\nabla_v m_{\rho\gamma}\right)\right) \\
\frac{\partial m_{\alpha\beta}}{\partial t} &= F^{-1}_{v\gamma}\nabla_v\left(m_{\alpha\beta}\frac{w_\gamma}{\rho(1-c)}\right) - m_{\gamma\beta}F^{-1}_{v\gamma}\nabla_v\left(\frac{w_\alpha}{\rho(1-c)}\right) - m_{\alpha\gamma}F^{-1}_{v\gamma}\nabla_v\left(\frac{w_\beta}{\rho(1-c)}\right) \\
&\quad -2\lambda\, m_{\alpha\gamma}\varphi_{m_{\gamma\beta}}
\end{aligned}
\tag{6.9}
$$

where

$$
F^{-1}_{\alpha\beta} = \frac{\partial Y_\alpha}{\partial r_\beta} \tag{6.10}
$$

$L_{\alpha\beta}=\frac{\varphi_{\alpha m_\beta}}{\varphi_{cc}}$ (see (5.11)) and $\nabla_\alpha=\frac{\partial}{\partial Y_\alpha}$, $D(c)=\frac{c^2(1-c)\varphi_{cc}}{\Lambda(c)}$ (see (I.10)), and $\frac{\tilde{\xi}(c)}{(1-c)^2}=\frac{\xi(c)}{c}$

(see (5.33)) is the relaxation time of **w**.

How shall we find the deformation tensor **F** ? We see three routes leading to its specification.

(i) By definition of the Lagrangian coordinates, **r**(**Y**) is a solution of $\frac{d\mathbf{r}}{dt}=-\frac{\mathbf{w}}{\rho(1-c)}$ with the initial condition $\mathbf{r}(0)=\mathbf{Y}$. We can thus transform (6.9) into a system of partial differential equations (second order in time) for **r** (**Y**,t), c (**Y**,t) and **m** (**Y**,t). We shall not follow this route since the resulting equations are very complex and very difficult to solve. Moreover, by solving them, we would obtain more information than we need. We do not need to know the trajectories **r** (**Y**, t) of all material points, we need only the local information about such trajectories expressed in the deformation tensor **F**.

(ii) From **F** we can construct the Finger tensor $\mathbf{FF}^T$ and adopt it as a new independent state variable. Equations (6.9) have to be thus extended into the system of four equations governing the time evolution of c, **w**, **m**, and $\mathbf{FF}^T$. This is indeed the clearest route to follow. We shall not follow it however here because we do not want to increase the complexity of (6.9). Rather, we shall follow the third route that is more phenomenological but by following it we are not increasing the mathematical complexity of the governing equations.

(iii) So far, we have not committed ourselves to a specific interpretation of the conformation tensor **m**. The commitment will be made in Section 6.5 where we shall specify the free energy density φ. We shall interpret **m** and specify φ in such a way that **m** will become directly related to the Finger tensor $\mathbf{FF}^T$. For the rest of this section, we shall consider $\mathbf{F}^{-1}$ appearing in (6.9) as a known function of **m** and c.

We end this section by reformulating (6.9) into a dimensionless form. We begin by partially specifying the free energy density φ. We recall that we have started our analysis of diffusion in [El Afif et al. (1999)] with a completely undetermined Helmholtz free energy Φ. The first step in its specification is Eq. (5.5) derived in Part I where we have

written Φ as a sum of the part that depends on $\mathbf{w}$ (the kinetic energy part) and the rest, that we have denoted $\int d\mathbf{r}\varphi(c,\mathbf{m})$, that is independent of $\mathbf{w}$. At this point it is thus φ that remains unspecified. It is clear that its complete specification requires a commitment to the physical interpretation of the conformation tensor $\mathbf{m}$. This, we shall do in Section 6.5. Here, we shall make only a partial specification that does not require yet the full commitment. If we ignore the concentration fluctuations and non-local effects, the density φ of the part of the free energy that is independent of $\mathbf{w}$ may be expressed as a sum of two contributions

$$\varphi(c,\tilde{\mathbf{m}}) = \varphi^{mix}(c) + \varphi^{cls}(c,\tilde{\mathbf{m}}) \tag{6.11}$$

where φ^{mix} is the mixing energy that may be approximated here by the well known Flory-Huggins [Flory (1953)] expression

$$\varphi^{mix} = \frac{RT}{\Omega_s}\left(\phi\ln\phi + \frac{(1-\phi)}{b}\ln(1-\phi) + \chi\phi(1-\phi)\right) \tag{6.12}$$

where R is the gas constant; T is the thermodynamic temperature, χ is the interaction parameter, b is the chain monomer number, Ω_s is the solvent molar volume, ϕ its volume fraction

$$\phi = a\,c \tag{6.13}$$

$a = \rho/\gamma_s$; γ_s is the solvent material density (assumed to be constant), ρ is the overall density (also assumed to be a constant). In the following, we will assume that b is large enough so that the terms involving 1/b will be ignored. The second term φ^{cls} on the right hand side of (6.11) stands for the contribution of the polymer to the elastic Helmholtz free energy, we shall write it as

$$\varphi^{cla}(\phi,\tilde{\mathbf{m}}) = \frac{G_0}{2}(1-\phi)h(\phi,\tilde{\mathbf{m}}) \tag{6.14}$$

where G_o is the modulus of elasticity i.e., $G_o = n_o k_B T$, n_o is the "elasticity density" of the dry polymer, [Beris et al. (1994)]; k_B is the Boltzmann constant and T is the thermodynamic temperature (assumed to be a constant). By $\tilde{\mathbf{m}}$ we denote the dimensionless conformation tensor $\tilde{\mathbf{m}} = \frac{\mathbf{m}}{z m_o}$, where z is normalization constant that will be specified in Section 6.5 and $m_o = k_B T/H$, where H is a characteristic elastic constant. The quantity $h(\phi,\tilde{\mathbf{m}})$ introduced in (6.14) remains at this point still unspecified. We shall specify it in Section 6.6.

Now, we proceed to the dimensionless formulation. We introduce the dimensionless space coordinate, time, c, w, and $\mathbf{m}$ as follows:

$$\bar{Y} = \frac{Y}{L_o}, \quad \nabla_\alpha = \frac{1}{L_o}\bar{\nabla}_\alpha, \quad \theta = \frac{t}{\tau_d}, \quad \frac{\partial}{\partial t} = \frac{1}{\tau_d}\frac{\partial}{\partial \theta},$$

$$C = \frac{c}{c_{eq}}, \quad \mathbf{W} = \left(\frac{\tau_d}{\rho c_{eq} L_o}\right)\mathbf{w}, \quad \mathbf{V} = \left(\frac{\tau_d}{L_o}\right)\mathbf{v}, \quad \tilde{\mathbf{m}} = \frac{\mathbf{m}}{z m_o} \tag{6.15}$$

L_o is a characteristic length scale in the material coordinates. τ_d is the characteristic time of diffusion at the initial state ($\tau_d = L_o^2/D_o$; $D(c,\mathbf{m})$ is the diffusion coefficient defined in (6.18) below; $D_o := D(C,\tilde{\mathbf{m}})|_{C=0,\tilde{\mathbf{m}}=\mathbf{I}}$). We use τ_d to scale the time. The governing equations (6.9) become

$$\frac{\partial C}{\partial \theta} = -F^{-1}_{v\alpha}\bar{\nabla}_v W_\alpha$$

$$\frac{\partial W_\alpha}{\partial \theta} = -F^{-1}_{v\beta}\bar{\nabla}_v(W_\alpha V_\beta) - \frac{1}{De(C)}\left(W_\alpha + \tilde{D}\,F^{-1}_{v\alpha}\left(\bar{\nabla}_v C + KC\,\tilde{L}_{\beta\gamma}(C,\tilde{\mathbf{m}})\bar{\nabla}_v \tilde{m}_{\beta\gamma}\right)\right)$$

$$\frac{\partial \tilde{m}_{\alpha\beta}}{\partial \theta} = F_{\nu\gamma}^{-1}\bar{\nabla}_{\nu}\left(\tilde{m}_{\alpha\beta}\frac{c_{eq}W_{\gamma}}{(1-c_{eq}C)}\right) - \tilde{m}_{\alpha\gamma}F_{\gamma\gamma}^{-1}\bar{\nabla}_{\nu}\left(\frac{c_{eq}W_{\beta}}{(1-c_{eq}C)}\right) - \tilde{m}_{\beta\gamma}F_{\nu\gamma}^{-1}\bar{\nabla}_{\nu}\left(\frac{c_{eq}W_{\alpha}}{(1-c_{eq}C)}\right)$$
$$-\frac{1}{zde(C)}\tilde{m}_{\alpha\gamma}h_{\tilde{m}_{\gamma\beta}} \qquad (6.16)$$

where c_{eq} is the equilibrium concentration at the solvent-polymer interface. This equilibrium concentration is obtained by solving $\Phi_c = 0$ and assuming the chemical equilibrium between the pure solvent and the solvent-polymer mixture. Since the chemical potential of the solvent is

$$\rho(\mu - \mu_0) = \varphi + (1-c)\varphi_c \qquad (6.17)$$

we arrive at the following expression for the mutual diffusion coefficient

$$D(c,m) = \frac{a(1-c)^2\varphi_{cc}}{\rho\tilde{\xi}(c)} \qquad (6.18)$$

where $\frac{\tilde{\xi}(c)}{(1-c)^2} = \frac{\xi(c)}{c}$ is the inverse of the relaxation time of the time evolution of w, $\tilde{D} = \frac{D}{D_0}$. In the equation governing the time evolution of w we have made the following transformation:

$$L_{\beta\gamma} = \frac{\varphi_{cm_{\beta\gamma}}}{\varphi_{cc}} = \frac{1}{azm_0}\frac{\varphi_{\phi\tilde{m}_{\beta\gamma}}}{\varphi_{\phi\phi}} = \frac{1}{zm_0}Kc\tilde{L}_{\beta\gamma}, \qquad (6.19)$$

where

$$\tilde{L}_{\beta\gamma} = \frac{-h_{\tilde{m}_\gamma} + (1-ac)h_{\phi\tilde{m}_\gamma}}{(1-2\chi ac) + Kac\left[(1-ac)h_{\phi\phi} - 2h_{\phi}\right]} \tag{6.20}$$

and

$$K = \frac{\Omega_s G_o}{2RT} \tag{6.21}$$

is a dimensionless parameter that measures the relative importance of the mixing and the elastic free energies. It also indicates the extent of the swelling. For large values of K, the elastic part of the free energy dominates the mixing contribution and consequently the polymer swelling is relatively small. On the contrary, small values of K correspond to large swelling since the mixing energy dominates the elastic recovery of the polymer chains. For methanol-PMMA glassy mixture (see Table 6.1), K=27.06 which means that the polymers swells less. The ratio K/De also indicates the importance of the coupling between the diffusion and the internal structure evolution equations.

In addition to K, the time evolution equations (6.16) involve two other dimensionless parameters De and de. The first, De, called a w-Deborah number, is defined as

$$De(C) = \frac{(1-c_{eq}C)^2}{\tilde{\xi}(C)\tau_d} \tag{6.22}$$

The second, de, called a m-Deborah number, is given by

$$de(C) = \frac{1}{\tilde{\lambda}(c)\tau_d} \tag{6.23}$$

where $\lambda = \dfrac{\tilde{\lambda}}{(1-\phi)G_0}$ is the inverse of the relaxation time of m. We recall that $\tau_d = L_0^2/D_0$, the diffusion coefficient $D(C,\tilde{m})$ is defined in (6.18), and $D_0 = D(0,1)$. We use the established terminology according to which "a quantity"-Deborah number equals $\tau_{\text{"a quantity"}}$

$_{\text{quantity}}/\tau_d$, where $\tau_{\text{"a quantity"}}$ is the relaxation time of "a quantity". Note that the Deborah number introduced in [Vrentas et al. (1975, 1977)] is essentially the m-Deborah number (6.23).

In the dimensionless formulation (6.16) the parameter space $\wp=(\Phi, \Lambda, \lambda)$ introduced in (5.7) in the general setting becomes a three dimensional space with coordinates (De, de K,). We can find a correspondence between regions in $\wp$ and types of diffusion. The correspondence, summed up in Figure 6.1 and Figure 6.2, is the following:

- De is small (Figure 6.1)
  - K « 1 Diffusion is driven by gradient of the solvent concentration c, the diffusion is Fickian (c-model, see Section 5.5.1 in Part I chapter 5)
  - K » 1 diffusion is driven by gradient of the polymer conformation tensor **m** , the swelling is small (**m**-model, see Section 5.4.1 in Part I chapter 5)
  - K ~1 diffusion is driven by gradient of the solvent concentration c and gradient of the polymer conformation tensor **m** ((c,**m**)-model, see Section 5.4 in Part I chapter 5)
    - de « 1 diffusion is viscous [Thomas et al. (1982)]]
    - de » 1 diffusion is elastic
    - de ~ 1 diffusion is viscoelastic [Durning et al. (1986), Wu et al. (1993)]
- De is large : super and hyper osmotic diffusion (Figure 6.2)
  - K/De « 1 perfect shock-waves ((c, w)-model , see Section 5.6 in Part I chapter 5)
  - K/De » 1 diffusion is with w-inertia and is driven by gradient of the polymer conformation tensor **m**
    - de « 1 diffusion is viscous
    - de » 1 diffusion is elastic
    - de ~ 1 diffusion is viscoelastic

- De intermediate : anomalous diffusion influenced by both K and de.

The models discussed in the literature [Thomas et al (1982), Durning et al. (1986), Wu et al (1993)] are situated clearly in the first category depicted in Figure 6.1. The experimentally observed Case II diffusion is reproduced in solutions of the governing equations of these models only if a glass-rubber transition is imposed in the choice of the parameters of the models (the parameters, functions of the solvent concentration, involve large jumps). This is indeed relevant if the polymer undergoes during the diffusion the glass-rubber transition. For this to happen, it is necessary that the temperature at which the observations are made (this is usually the room temperature) is close to the glass transition temperature. If the polymer-solvent mixture does not undergo any glass-rubber transition during the diffusion [Thomas et al. (1978), Barriere (1997)] (observed for polymers with the glass transition temperature that is larger than the temperature of the observation), then there is no reason to introduce into the models parameters involving large jumps in their dependence on the solvent concentration. The parameters entering the models are in this case constants independent of the solvent concentration. But with such parameters, solutions of the governing equations of the classical Case II models do not show the experimentally observed Case II behavior. On the other hand, the models corresponding to the region depicted in Figure 6.2 do imply the experimentally observed Case II behavior even if the parameter entering the model are independent of the solvent concentration.

Let us now make a few comments about the dependence of Λ, λ and D on c. As we said above, in the specific illustrations that we shall present below in Section 6.6, we shall choose them to be constants independent of c. But, if they are not constants, how do they depend on c? It has been suggested in [Thomas et al. (1982), Fu et al (1993), Wu et al (1993)] to let the diffusion coefficient to increase exponentially with the concentration

$$\tilde{D}(C,\tilde{m})=\frac{D(C,\tilde{m})}{D_0}=\exp(kC) \tag{6.24}$$

where $D_0 = D(0,1)$ is the diffusion coefficient of the polymer at the initial state (e.g. glassy state) and k is a constant in which the individual features of the polymer is expressed. Typical values attributed to k/c_{eq} range from 1 to 20 [Thomas et al. (1982) Wu et al. (1994)] to fit the collected data on methanol-poly(methyl methacrylate). On the same footing, we assume that the relaxation time inverses vary as

$$\tilde{\tilde{\xi}}(C)=\frac{\tilde{\xi}(C)}{\tilde{\xi}(0)}=\exp(n\,C) \tag{6.25}$$

$$\tilde{\tilde{\lambda}}(C)=\frac{\tilde{\lambda}(C)}{\tilde{\lambda}(0)}=\exp(gC) \tag{6.26}$$

where n and g are material constants.

In order to estimate De and de we need to know the characteristic times of the relaxation. To estimate them, we shall use the analysis developed in the context of the (c,w)-model in Part I. We have introduced there the diffusion Mach number

$$M_{diff}=\frac{V}{\sqrt{\kappa}} \tag{6.27}$$

where v is the velocity of the fluid and $\sqrt{\kappa}$ is the osmotic speed that is, now in the context of the (c,w,m)-model (see (6.7)), given by $\sqrt{\kappa}=\sqrt{\frac{1}{\rho}\left[c\varphi_{\infty}+\frac{cm}{1-c}\varphi_{cm}\right]}$. The w-Deborah number defined by Eq. (6.27) becomes thus

$$De(C)=\frac{(1-c_{eq}C)^2}{\tilde{\xi}(c)\tau_d}=\left(\frac{D_0(1-c_{eq}C)}{\sqrt{\frac{(c\varphi_{\infty})_0}{\rho}}L_0}\right)^2 e^{-nC} \tag{6.28}$$

Using the fact that $\sqrt{\frac{1}{\rho}(c\varphi_{\infty})_0}=\lim_{c\to 0}\sqrt{\frac{c\varphi_{\infty}}{\rho}}=\lim_{c\to 0}\frac{\sqrt{\kappa}}{\sqrt{1+\frac{K\tilde{m}c}{z(1-c)}\tilde{L}}}$ and in view of (6.28), we obtain

$$De(C)=\left(\frac{D_0M_{diff,0}(1-c_{eq}C)}{v_0L_0}\right)^2 e^{-nC} \tag{6.29}$$

In Case-II diffusion, the velocity of the propagation is constant. Assuming that v_0 equals approximately D_0/L_0, we arrive at the following expression

$$De(C)\approx\left(M_{diff,0}(1-c_{eq}C)\right)^2 e^{-rC} \tag{6.30}$$

$M_{diff,0}$ constitutes now the parameter to be adapted for the different regions of diffusion.

Regarding the m-Deborah number de, we follow [Vrentas et al. (1975, 1977), Wu et al (1993)],

$$d\epsilon(c) = \frac{1}{\tilde{\lambda}(c)\tau_d} = \frac{\eta(c)D_o}{G_oL_o^2} = \frac{\eta_0 D_o}{G_oL_o^2} e^{-\varepsilon c} \tag{6.31}$$

η is the viscosity of the polymer and G_o its elastic modulus.

6.5. Free Energy

The free energy Φ with which we have started in Part I was completely unspecified. We have partially specified it in (5.5) and then in (6.11)-(6.14). What remains unspecified in the free energy at this point is thus $h(\phi,\tilde{\mathbf{m}})$ introduced in (6.14) in the elastic part φ^{ela}. The specification of $h(\phi,\tilde{\mathbf{m}})$ has to begin with the following question: what is the precise physical meaning of the conformation tensor $\mathbf{m}$ that is serving us as a state variable describing the internal structure of the polymer medium? We shall now answer this question. Let the macromolecules composing the polymeric medium be modeled as dumbbells with the end-to-end vector $\mathbf{R}$. When the polymeric medium is completely dry, i.e. when $\phi = 0$, then deformations of the molecules are completely translated into the macroscopic deformations. We shall express it by writing $\mathbf{R}=\mathbf{R}^{(macro)}$, where $\mathbf{R}^{(macro)}$ is the macroscopic displacement vector. As the diffusion proceeds, the polymeric medium becomes less rigid, the macromolecules composing it are more independent one of the other, and consequently, their deformations do not translate completely into the macroscopic deformations. We shall thus have

$$\mathbf{R}=\sqrt{f(\phi)}\mathbf{R}^{(macro)} \tag{6.32}$$

where $\sqrt{f(\phi)}$ is a dimensionless phenomenological function satisfying the following properties: $f(0)=1$ and $f(\phi)<1$ if $\phi>0$. In this paper, we shall choose $f(\phi)$ to be

$$f(\phi)=1-\frac{\phi}{\phi_{eq}}+\left(\frac{\phi}{\phi_{eq}}\right)\frac{1}{tr\tilde{m}_{eq}} \tag{6.33}$$

where $\tilde{m}_{eq} = \tilde{m}_{eq}\delta$ is the dimensionless conformation tensor at the end of the diffusion process (i.e. at $\phi=\phi_{eq}$), δ is the unit tensor. The dimensionless conformation tensor $\tilde{m}$ is now interpreted as

$$\tilde{m}_{\alpha\beta} = <\tilde{R}_{\alpha}^{(macro)}\tilde{R}_{\beta}^{(macro)}> = F_{\alpha\nu}F_{\beta\nu} \tag{6.34}$$

where $\tilde{R} = R/\sqrt{m_o}$ and F is the deformation tensor introduced in (6.10).

What remains now is to suggest the free energy of a system composed of dumbbells. We shall make two most obvious and simplest choices. First, we regard the dumbbells as the elastic Hookean dumbbells [Bird et al. (1977)] (Maxwell model), and second, we regard them as finitely extensible dumbbells [Bird et al. (1977), Grmela et al. (1986)] (FENEP model). The modified free energy corresponding to the Maxwell model is (we use the usual form of the free energy written in terms of <RR> and then use (6.32) to rewrite it as a function of $\tilde{m}$)

$$h(\phi,\tilde{m}) = tr(f(\phi)\tilde{m}) - \ln\left(\det\left(f(\phi)\tilde{m}\right)\right) \tag{6.35}$$

and to the FENEP model

$$h(c,\tilde{m}) = -\tilde{R}_0^2 \ln\left(1-\frac{tr(zf(\phi)\tilde{m})}{\tilde{R}_0^2}\right) - \ln\left(\det\left(zf(\phi)\tilde{m}\right)\right) \tag{6.36}$$

where R_0 is the maximal extensibility of the dumbbell , $\tilde{R}_o = \frac{R_o}{\sqrt{m_o}}$ is a dimensionless quantity, expressed in terms of m_o defined above and R_o. The normalization parameter z is now

$$z=\left(\frac{\tilde{R}_0^2}{1+\tilde{R}_0^2}\right) \tag{6.37}$$

(note that z=1 in the context of Maxwell model). We note that in the limit $\tilde{R}_0 \to \infty$, i.e. in the limit when the finite extensibility becomes infinite, the FENEP free energy (6.36) becomes the Maxwell free energy (6.35).

By inserting (6.35) into (6.16) we obtain

$$\frac{\partial C}{\partial \theta}=\left.\frac{\partial C}{\partial \theta}\right|_{\text{Eq.(6.16)}}$$

$$\frac{\partial W_\alpha}{\partial \theta}=\left.\frac{\partial W_\alpha}{\partial \theta}\right|_{\text{Eq.(6.16)}}$$

$$\frac{\partial \tilde{m}_{\alpha\beta}}{\partial \theta}=F_{v\gamma}^{-1}\overline{\nabla}_v\left(\tilde{m}_{\alpha\beta}\frac{c_{eq}W_\gamma}{1-c_{eq}C}\right)-\tilde{m}_{\alpha\gamma}F_{v\gamma}^{-1}\overline{\nabla}_v\left(\frac{c_{eq}W_\beta}{1-c_{eq}C}\right)-\tilde{m}_{\gamma\beta}F_{v\gamma}^{-1}\overline{\nabla}_v\left(\frac{c_{eq}W_\gamma}{1-c_{eq}C}\right) \tag{6.38}$$
$$-\frac{1}{de(C)}\left(f(C)\tilde{m}_{\alpha\beta}-\delta_{\alpha\beta}\right)$$

The internal elastic stress tensor, given for a general free energy in the formula (5.8), becomes

$$\sigma_{\alpha\beta}^{cla}=G_o\left(1-ac_{eq}C\right)\left(f(C)\tilde{m}_{\alpha\beta}-\delta_{\alpha\beta}\right) \tag{6.39}$$

By inserting (6.36) into (6.16) we obtain

$$\frac{\partial C}{\partial \theta}=\left.\frac{\partial C}{\partial \theta}\right|_{\text{Eq.(6.16)}}$$

$$\frac{\partial W_\alpha}{\partial \theta}=\left.\frac{\partial W_\alpha}{\partial \theta}\right|_{\text{Eq.(6.16)}}$$

$$\frac{\partial \tilde{m}_{\alpha\beta}}{\partial \theta} = F_{v_1}^{-1}\overline{\nabla}_v\left(\tilde{m}_{\alpha\beta}\frac{c_{eq}W_\gamma}{1-c_{eq}C}\right) - \tilde{m}_{\alpha\gamma}F_{v_1}^{-1}\overline{\nabla}_v\left(\frac{c_{eq}W_\beta}{1-c_{eq}C}\right) - \tilde{m}_{\gamma\beta}F_{v_1}^{-1}\overline{\nabla}_v\left(\frac{c_{eq}W_\alpha}{1-c_{eq}C}\right)$$
$$-\frac{1}{zde(C)}\left(\frac{z\tilde{R}_o^2 f(C)}{\tilde{R}_o^2 - tr\left(zf(C)\tilde{m}\right)}\tilde{m}_{\alpha\beta} - \delta_{\alpha\beta}\right) \qquad (6.40)$$

and the internal elastic stress tensor

$$\sigma_{\alpha\beta}^{ela} = G_o\left(1-ac_{eq}C\right)\left(\frac{zf(C)\tilde{R}_0^2}{\tilde{R}_0^2 - tr\left(zf(C)\tilde{m}\right)}\tilde{m}_{\alpha\beta} - \delta_{\alpha\beta}\right) \qquad (6.41)$$

Before turning to numerical solutions of (6.38) and (6.40), we shall return briefly to Section 5.4 in Part I, chapter 5. Our objective now is to make the results obtained there for a general free energy more explicit by inserting into them the Maxwell free energy (6.35). The resulting governing equations will be then directly comparable with the governing equations used in [Wu et al (1993)]. As argued in Section 5.4. of Part I, the governing equations (5.7) reduce in the region of the parameter space $\wp$ corresponding to De<<1 to Eqs. (5.9). Now, we can be more specific. We replace Eqs. (5.7) by their more specific and dimensionless reformulation (6.16). Moreover, we introduce into them the Maxwell free energy (6.35), and we limit ourselves to one dimension. After simple calculations, we arrive at a nonlinear time evolution equation for the extra stress tensor. As a next step, we drop the nonlinear terms and reduce the description to one dimension. We obtain

$$\frac{\partial \sigma}{\partial t} + \tilde{\lambda}\sigma = G_0\frac{\partial v_p}{\partial x} \qquad (6.42)$$

where v_p = - w/ρ(1-c) is the polymer velocity. In the limit of small deformations $\varepsilon = F_{11} - 1$, and we thus arrive at

$$\frac{\partial c}{\partial t} = F_{11}^{-1}\frac{\partial}{\partial Y}\left[DF_{11}^{-1}\left[\frac{\partial c}{\partial Y} + L_{c\sigma}\frac{\partial \sigma}{\partial Y}\right]\right]$$

$$\frac{\partial \sigma}{\partial t} + \tilde{\lambda}\sigma = G_o\left(\frac{\partial F_{11}}{\partial t}\right) \qquad (6.43)$$

where $L_{c\sigma} = \frac{1}{G_o}L_{cm}$. These equations are identical with the governing equations of the linear viscoelastic Maxwell model derived in [Wu et al. (1993)] provided we use $F_{11} = \frac{1}{1-c}$ that they themselves propose to use for the inverse of the deformation tensor. The model (6.43), extending the linear viscoelastic models derived in [Thomas et al. (1982), Durning et al. (1986)] captures many features of Case II diffusion that is accompanied with significant changes in properties (like the diffusion and viscosity coefficients considered as phenomenological functions of the solvent concentration) of the polymeric medium. The model does not provide however a setting for a clear understanding the front propagation. As we see in this paper, such setting is obtained by adopting the diffusion flux w into the set of independent state variable.

In the three dimensional analysis, the relation (6.41) between the stress tensor σ and $\tilde{m}$ cannot be inverted. The third equation in (6.40) cannot be thus replaced by an equation governing the time evolution of σ. In the one dimensional analysis however the formula (6.41) can be inverted. We obtain easily $\tilde{m} = \frac{(\sigma + G_o)\tilde{R}_o^2}{z(\sigma + G_o(1+\tilde{R}_o^2))}$. Inserting this expression into the third equation in (6.40), we arrive at

$$\frac{\partial \sigma}{\partial t} + \tilde{\lambda}\left(1 + \frac{1}{\tilde{R}_0^2}\left(1 + \frac{\sigma}{G_o}\right)\right)^2\sigma = -\left(1 + \frac{1}{\tilde{R}_0^2}\left(1 + \frac{\sigma}{G_o}\right)\right)\frac{\partial(\sigma v_p)}{\partial x} + G_0\left(1 + \frac{1}{\tilde{R}_0^2}\left(1 + \frac{\sigma}{G_o}\right)\right)\left(1 + \frac{2\sigma}{G_o}\right)\frac{\partial v_p}{\partial x}$$
$$+ \frac{v_p}{\tilde{R}_0^2}\left(1 + \frac{\sigma}{G_o}\right)\frac{\partial \sigma}{\partial x}$$

(6.44)

In the limit of small deformations, the strain is given by $\varepsilon = F_{11} - 1$. Ignoring the non-linear terms involved in (6.44), FENEP-diffusion model becomes

$$\frac{\partial c}{\partial t} = F_{11}^{-1}\frac{\partial}{\partial Y}\left[DF_{11}^{-1}\left[\frac{\partial c}{\partial Y} + L_{c\sigma}\frac{\partial \sigma}{\partial Y}\right]\right]$$

$$\frac{\partial \sigma}{\partial t} + \lambda\left(1+\frac{1}{\tilde{R}_o^2}\right)\sigma = G_o\left(1+\frac{1}{\tilde{R}_o^2}\right)\left(\frac{\partial F_{11}}{\partial t}\right) \qquad (6.45)$$

where now $L_{c\sigma} = \frac{\tilde{R}_o^4 G_o}{z\left(G_o\left(\tilde{R}_o^2+1\right)+\sigma\right)^2}L_{cm}$. Equations (6.44) or their approximation (6.45) are thus direct extensions of the governing equations (6.43) [Wu et al. (1993)] towards a more realistic rheology (the Maxwell-model rheology is replaced by the FENEP-model rheology). It is obvious that if $\tilde{R}_o \to \infty$, we recover from (6.45) the governing equations (6.43).

6.6. Numerical Solutions

We turn our attention now to the one-dimensional diffusion into a thin film of a glassy polymer immersed in a solvent. This type of diffusion was studied experimentally for example in [Alfrey et al (1966)] (polystyrene immersed in acetone), [Kwei et al. (1969)] (cross-linked epoxies immersed in benzene) and [Thomas et al. (1978)] (poly (methyl-methacrylate) immersed in methanol). Our objective is to reproduce the experimental observations as solutions of the governing equations of (c,w,m)-model.

It will be more convenient for numerical calculations to rewrite (6.38) or (6.40) in the state variables (C, V, $\tilde{m}$), where $V=\frac{W}{C}$ is the dimensionless solvent velocity. The second equation in (6.38) or (6.40) becomes

$$\frac{\partial V_\alpha}{\partial \theta} = -V_\beta F_{v\beta}^{-1} \overline{\nabla}_v V_\alpha - \frac{1}{De(C)} \left(V_\alpha + \tilde{D} F_{v\beta}^{-1} \left(\overline{\nabla}_v \ln C + K \tilde{L}_{p_\gamma} (C, \tilde{m}) \overline{\nabla}_v \tilde{m}_{p_\gamma} \right) \right) \qquad (6.46)$$

The equations governing the time evolution of the solvent concentration and the conformation tensor will remain unchanged except that W is replaced by CV.

We shall assume that the initial thickness of the sample, $2L_0$, is negligible if compared with the surface, S, of the film, i.e. $2L_0 << \sqrt{S}$. The process of sorption into a thin film is a symmetric process; i.e., the solvent enters the polymer from opposite sides and diffuses to the center of the film. We can therefore study only the half-thickness of length L_0 [Wu et al. (1993)]

6.6.1. Initial and Boundary Conditions

We know from experimental observations of Case II diffusion [Alfrey et al. (1966), Thomas et al. (1978)] that the weight gain of the polymer evolves linearly in time. This linear kinetics is observed to be always preceded by an induction period during which the solvent does not penetrate the core of the polymer and the weight gain of the polymer is negligible. This observed induction period indicates that the core is 'resisting' the penetration of the solvent molecules until the interface reaches a state of certain equilibrium. Inspired by these observations, we conjecture that the process of absorption that takes place at the interface is different from Case II diffusion taking place at the core of the film. We decide therefore to treat separately the surface and the core. In both cases we shall use (c,v,m)-model but the parameters (De,de,K) used at the surface will be different from the parameters (De,de,K) used in the core. In the following, we shall denote the diffusion Mach number at the surface by Ms and the diffusion Mach number in the core by Mc. We use the same subscripts for the Deborah numbers; i.e., respectively, Dec, dec for the core and Des, des for the surface. In this paper we shall limit ourselves to $K_c=K_s=K$.

Let $\Xi(\overline{Y}, \theta) = (C(\overline{Y}, \theta), V(\overline{Y}, \theta), \tilde{m}(\overline{Y}, \theta))$ designate the one dimensional and dimensionless set of state variables. Since the polymer is initially dry, the concentration C, the mass flux, and the velocity of the solvent, V, are equal to zero within the whole polymer film. The dimensionless conformation tensor describing the polymer is the unit tensor. From this initial state, the system evolves, as the time goes to infinity, to a final equilibrium state. The initial conditions are the following: $\Xi(\overline{Y}, 0) = (0, 0, 1)$ for all $\overline{Y} \in [0, 1]$ in the dry polymer. At the interface, i.e. at $\overline{Y} = 0$, the set of state variables is given by $\Xi(0, \theta) = (C(0, \theta), V(0,\theta), \tilde{m}(0, \theta))$ for all θ . The time evolution of $C(0,\theta)$,$V(0,\theta)$, and $\tilde{m}(0,\theta)$ is governed by (c,w,m)-model with the parameters (Ms, des, K). The numerical resolution requires the knowledge of the values of the state variables in the region containing initially only the solvent; that is in $\overline{Y} < 0$ ($\overline{Y} \in [0, 1]$ represents the coordinate in half thickness of the polymer film). In the material coordinates, we denote by $\overline{Y} = 0^-$ the space coordinate near the surface initial position but on the side of the solvent. The equilibrium concentration reached at the end of the induction period is c_{eq}. This is then taken to be the concentration at $\overline{Y} = 0^-$ for all θ. The knowledge of the velocity and the conformation tensor at $\overline{Y} = 0^-$ needs the knowledge of the time at which the polymer has swelled in the solvent region and reached the position $\overline{Y} = 0^-$. Let θ_o be such time. When $\theta < \theta_o$ the polymer is assumed to have not yet swelled to reach this position (i.e. $\overline{Y} = 0^-$); consequently, the solvent fluid still remains unperturbed and its velocity equals zero. The conformation tensor also vanishes since there is no polymer in the solvent region at $\overline{Y} = 0^-$. When $\theta \geq \theta_o$ the polymer begins to occupy regions in the solvent at $\overline{Y} \leq 0^-$. In that case, the velocity as well as the conformation tensor are assumed to be equal to their respective values attained at the surface. The gradients of velocity and of the conformation tensor vanish at the interface. This is because when $\theta \geq \theta_o$ at $\overline{Y} \leq 0^-$, the set of state variables has already reached the equilibrium state. Since 0^- is of the order of the surface thickness, we have chosen it in our numerical calculations to be $\delta \approx 0.1\text{-}0.2\ \mu m$. The time θ_o is estimated by using the

following equation: $L(\theta_o)-L_o \approx \delta$, at $\theta=\theta_o$ and at $\bar{Y}=0$. The swelling of the half thickness of the polymer, related to the linear macroscopic deformation, is of the order of the surface thickness δ. The polymer thickness (already swolien) $L(\theta)$ at time θ is calculated from Eq.(6.54).

In summary, the set of the state variables at the material position located just behind the initial position of the polymer in the solvent region is

$$\Xi(\bar{Y},\theta)|_{\bar{Y}=0-,\theta<0} = (1, 0, 0) \qquad \text{if} \quad (L(\theta)-L_o) < \delta$$

$$\Xi(\bar{Y},\theta)|_{\bar{Y}=0-,\theta\geq 0} = (1, V(0,\theta), \tilde{m}(0,\theta)) \qquad \text{if} \quad (L(\theta)-L_o) \geq \delta$$

It is worth to mention, that a second order evolution equation for the solvent concentration, c, can be derived from the family of equations (6.16). This is because if we ignore the first term on the right hand side of second equation of Eqs. (6.16), the three terms on the right hand side of the third equation of (6.16) and assume in addition that the parameters of the model, i.e., De, D, E=DL, are constants, we arrive at

$$\frac{\partial^2 C}{\partial \theta^2}+\frac{1}{De}\frac{\partial C}{\partial \theta}=\frac{1}{De}\frac{\partial^2 C}{\partial \bar{Y}^2}+\frac{E}{De}\frac{\partial^2 \tilde{m}}{\partial \bar{Y}^2} \tag{6.47}$$

$$\frac{\partial m}{\partial \theta}=-\frac{1}{zde}\tilde{m}h_{\tilde{m}}$$

where De and de are respectively the w- and the m-Deborah numbers defined above. One notices then that the Long and Richman equations governing the interface time evolution [Long et al. (1960)] are (6.47) in which the two terms on the right hand side of the first equation of (6.47) are neglected, i.e.

$$C(\theta)=C_0+(C_\infty-C_0)(1-e^{-De\theta}) \tag{6.48}$$

C_0 is the dimensionless initial concentration; C_∞ is the normalized equilibrium concentration.

6.6.2 Results

In our numerical illustration, we aim at Case II diffusion during which the polymer does not undergo the glass-rubber transition. Such diffusion has been observed in glassy polymers [Thomas et al. (1978), Barriere (1997)]. The phenomenological parameters D, Λ and λ in which we express the individual features of the systems under consideration will be chosen to be constants independent of the solvent concentration (this means that in (6.24), (6.29) and (6.31) we put k=n=g=0). We use the finite difference method to discretize the partial differential equations (6.46) and the first and third equations in (6.38) and (6.40). We use the non-conservative first order upwind scheme [Hirsch (1997)] that seems to be sufficient for our numerical study. It is useful to note that the Rankine-Hugoniot relation (see (5.26) in Part I) can still be applied for the solvent mass conservation equation, since it is a conservation equation. This relation, in its dimensionless form, is $[CV]_i = s_i[C]_i$, where $[A]_i=A_i-A_{i-1}$. s_i is equal to the dimensionless shock or discontinuity speed at the grid point i [Hirsch (1997)] and is given by

$$s_i = \begin{cases} \dfrac{(CV)_i - (CV)_{i-1}}{C_i - C_{i-1}} & \text{if } C_i \neq C_{i-1} \\ \dfrac{1}{2}(V_{i-1} + V_{i+1}) & \text{if } C_i = C_{i-1} \end{cases} \tag{6.49}$$

The dimensionless length of the film has been divided into one hundred grid points. The calculations have been executed on a 333 Hz PC computer using the Matlab software.

We start the computations, for the sake of simplicity, with an initial solvent concentration of the order of 10^{-8}. The conformation tensor, the velocity and the concentration profiles, are calculated, in this succession at each time step. Once the profiles of the concentration are obtained, we determine the mass uptake from

$$\frac{M(t)}{M_{eq}} = \frac{\int_0^{L_o} cFdY}{c_{eq}F_{eq}L_o} \tag{6.50}$$

F, the deformation tensor, is related to the dimensionless conformation tensor as follows

$$\tilde{m}_{\alpha\beta} = F_{\alpha\nu}F_{\beta\nu} \tag{6.51}$$

which becomes in the one dimensional study

$$F = \sqrt{\tilde{m}} \tag{6.52}$$

Having calculated the profiles of the concentration, of the velocity and of the conformation tensor, the determination of the extra stress tensor σ and the polymer gradient velocity becomes a straightforward task. We are then also able to calculate the internal longitudinal viscosity

$$\eta_l(c) = -\frac{\sigma}{\dot{\varepsilon}_p} \tag{6.53}$$

where σ is the polymer elastic extra stress tensor, and $\dot{\varepsilon}_p$ is the strain rate (gradient of the polymer velocity). This calculated viscosity can be now compared with the viscosity that constitutes a part of the input of classical Case II models [Thomas et al. (1982), Fu et al. (1993), Wu et al, (1993)]. It has been noticed that in order to reproduce the basic features of Case II diffusion, in the context of the classical Case II models, the viscosity has to be

assumed to be very strongly decreasing function of the solvent concentration c. We recall that we have not made at the outset of our numerical analysis any assumption of this type. The phenomenological parameters with which we have started (i.e. the diffusion coefficient, viscosity coefficient, and the relaxation times) are constants independent of the solvent concentration.

All the results presented below are calculated for both the Maxwell and the FENEP free energies and for the methanol-poly (methyl metacrylate) mixture properties listed in Table 6.1. The curves in Figures 6.1 to 6.10 are those corresponding to Maxwell viscoelastic model, and Figures 6.11 to 6.14 exhibit results obtained from the FENEP model.

Figure 6.3 shows the concentration of the surface versus time for (Ms, Mc) = (1,1), (3.35,1), (3.35,3.35), (3.35,6.9), and (6.9,6.9) (respectively from left to right). To recover Case-II diffusion, Ms has to be smaller than Mc. If this is the case then there is an initial period during which the surface absorbs slowly the solvent. Following this initial period, there is a rapid increase of the concentration that is followed by a plateau corresponding to the equilibrium value of the concentration (this is observed more clearly in the third and the fourth curves). This phenomenon has been identified as a weak autocatalytic response of the surface to penetration [Thomas et al. (1982), Hui et al (1987), Fu et al. (1993)].

The concentration profiles against the normalized polymer length are shown in Figure 6.4 for (Ms Mc) =(3.35, 6.9) (continuous lines) and (6.9, 6.9) (dashed lines). The calculated curves appear to be step-like for (3.35, 6.9); we also observe the absence of the concentration gradients behind the moving front which is in agreement with the familiar experimental observations reported for Case-II diffusion. Numerical calculations show that increasing Mc while keeping Ms smaller leads to sharper concentration profiles. Moreover, we see that by increasing Mc we increase the time needed for the completion of the sorption. To recover Case II diffusion, Ms must be relatively small and Mc relatively large. An increase of both Ms and Mc leads to diffusive concentration profiles

and thus to a feature that is not characteristic of Case II diffusion. This result supports our strategy to treat separately the core and the surface.

In Figure 6.5, we present the normalized mass-uptake curve versus time (in hours) for (Ms, Mc) = (1,1), (3.35,1), (3.35,3.35), (3.35,6.9), (3.35,20), and (6.9,6.9) (respectively from left to right). The curves calculated for (3.35,6.9), (3.35,20) are typical of Case II linear kinetics. The calculated curve for (3.35,6.9) reproduces the experimental curve (drawn in (•)) reported in [Thomas et al. (1978]. We know from the calculations that if Mc decreases (and then Dec) the velocity of the propagation of the front increases and therefore the time needed to complete the complete the penetration is reduced.

Figure 6.6 shows the velocity profiles versus the normalized length for (Ms, Mc)= (3.35,6.9), (continuous lines) and (6.9,6.9) (circles). The value of the velocity at the front is about 2-2.2 nm/s that corresponds to the choice of Ms=3.35. Following the suggested terminology, we may say that diffusion is super-osmotic. The experimental value for the velocity front is ~1.8 nm/s at 24 C [Thomas et al. (1978)]. From our simulation, an increase of Ms leads to a decrease of the velocity front value. However, increasing Ms while keeping Mc constant, will lead to diffusive concentration profiles as shown in Figure 6.4 and in Figure 6.6. Since the (6.9, 6.9) curve shows that the solvent front accelerates, but decelerates at the final stages of the sorption.

Figure 6.7 shows the profiles of the conformation tensor against the normalized length for (Ms, Mc) =(3.35, 6.9) (continuous lines) and (6.9, 6.9) (dashed lines). The dimensionless initial value of the conformation tensor was 1 for both the Maxwell and the FENEP free energies. The polymer evolves, due to the penetration by solvent, to a final swollen configuration. This state is calculated at each time step in which it is assumed that the final equilibrium conformation m_{eq} of the whole polymer equals to the equilibrium conformation at the surface. The numerical calculation leads, for (3.35, 6.9), to a value of the order of m_{eq}=1.3 and for (6.9, 6.9) to m_{eq}=1.16. des (the surface m-Deborah number) has been chosen to be larger than dec (the core m-Deborah number). The swelling is calculated using the following expression

$$\frac{L}{L_o} = \int_0^1 F d\bar{Y} \tag{6.54}$$

This is shown in Figure 6.8 for (Ms, Mc) = (1,1), (3.35,20), (3.35,6.9), (3.35,3.35), (6.9,6.9), and (3.35,1) (from top to bottom). The experimental curve in [Thomas et al. (1978)], which is drawn in (•), coincides exactly with the curve calculated for (3.35, 6.9). The volume increase of the polymer, as expected, follows the same kinetics as the mass uptake. This kinetics for (3.35, 6.9) and (3.35, 20) is similar to the typical Case II kinetics as seen in experimental observations.

The elastic extra stresses, created during the diffusion, are calculated for (Ms, Mc)= (3.35, 6.9) and are plotted in Figure 6.9. We notice that the profiles attain their maxima at the front, showing that the stresses are localized at the solvent moving boundary, while behind and ahead of the front the polymer is stress free. The amplitude of the Case II stresses varies from 7 to 13 MPa. The maximum value of the stress is attained at the interface and is of the order of 400 MPa. This value is higher than the value required to initiate a fracture. The same behavior is obtained using the FENEP free energy. For small values of $\tilde{R}_0$, the stresses are however found to be slightly larger. We recover the same order of magnitude provided by the Maxwell free energy if $\tilde{R}_0 > 15$. The polymer velocity gradients behave similarly, as shown in Figure 6.10. This is due to the sharp profiles of both the concentration and of the velocity of the solvent and also of the polymer conformation.

Figure 6.11 shows the curves of normalized internal longitudinal viscosity versus normalized concentration. These curves are obtained using Eq. (6.53) at a fixed spatial position but during the whole evolution of the state variables; i.e., $\eta_l\left(c(t)|_{Y\text{fixed}}\right) = -\dfrac{\sigma(t, Y\text{ fixed})}{\dot{\varepsilon}_p(t, Y\text{ fixed})}$. We also calculated the viscosity, but for fixed time and varied position. The calculation leads approximately to the same results. However, to see the real variation of the viscosity with the concentration or the rate of deformation, we think that the first procedure is more appropriate. For the Case II behavior, the viscosity

decreases slightly with concentration. The same is then true for the relaxation time of the internal structure. This is reasonable, since the polymeric chains gain in the process of diffusion some flexibility. However, the normalized viscosity is seen to fall only 5 to 20 times. In the classical Case II models, it has been assumed to decrease 100 to 1000 times. The behavior is typical of Case II diffusion is implied by (c,w,m)-model even for constant constitutive equations (viscosity, diffusion coefficient, relaxation times). For (Ms, Mc) =(6.9, 6.9), i.e. for the diffusion, shown in Figures 6.4, 6.5 and 6.6, that is not of Case II-type, the viscosity has been found to decrease with concentration about 1000. In Figure 6.11, the viscosity profiles were calculated using the Maxwell free energy. We have observed that the behavior shown in Figure 6.11 will appear even with the FENEP free energy if $\tilde{R}_o>15$. This indicates the importance of the choice of the free energy in modeling the non-Fickian diffusion. Figures 6.12 and 6.14 show the viscosity versus gradient of the polymer velocity respectively for Maxwell and FENEP free energies. We believe that the behavior of the viscosity for higher deformations arising in our calculations is probably due to the asymmetric shapes of both the stresses and the gradient of the polymer velocity with respect to their maxima.

Figure 6.15 shows the curves of the polymer volume increase versus time calculated using the FENEP free energy with $\tilde{R}_o$=1, 1.5, 2, 3.5, 5 and 15 (from bottom to top) for (Ms, Mc)=(3.35, 6.9). The value of $\tilde{R}_o$ is shown to control the degree of swelling of the polymer. Similarly, Figure 6.16 shows the curves of the normalized polymer weight gain versus time calculated using the FENEP free energy with $\tilde{R}_o$=1, 1.5, 2, 3.5, (from left to right) for (Ms,Mc)=(3.35, 6.9). We see that the time needed to complete the penetration is influenced slightly by the value of $\tilde{R}_o$.

6.7. Conclusion

In this and the previous paper we have introduced a new model of both the standard and nonstandard isothermal diffusion of a solvent into a polymer in overall mechanical

equilibrium. We call it a (c,w,m)-model since the quantities that play in it the role of independent state variables are the solvent concentration c, the diffusion flux w, and a symmetric tensor m characterizing the internal structure of the polymeric medium. The individual nature of the solvent-polymer system is expressed in it in the free energy, the relaxation time of the polymeric structure, and the relaxation time of the diffusion flux.

The process of finding solutions of the governing equations begins with properties of solutions that can be found before making commitment to a specific choice of the free energy. Such properties are: (i) reductions to simpler, previously known or new, models, and (ii) wave propagation. The first type of properties has been systematically studied in particular in Part I. We have derived many simpler models (among them for example the classical Fickian model and the classical Case II models) that are well known from previous considerations and, in addition, one new model called (c,w)-model. The second type of properties are properties of the wave-type propagation of disturbances in the solvent concentration. We call them osmotic waves since they are analogous to sound waves in compressible simple fluids (solvent concentration and osmotic pressure play the role of the mass density and the fluid pressure). We are also able to find, by analytical methods, an information about possible formation of discontinuities during the diffusion. In particular, we predict this type of behavior also in polymers that do not experience glass-rubber transitions (see [Thomas et al. (1978), Barriere (1997)] where this type of diffusion has been observed).

Detailed solutions of the governing equations of the (c,w,m)-model, reported in Section 6.6, are found by using numerical methods. In the numerical analysis we have to, of course, specify completely the free energy Φ. We make two choices: the Maxwell free energy and the FENEP free energy. Both are appropriately modified to take into account the swelling. It is important to emphasize that other, more realistic, choices of Φ could be made without increasing substantially the complexity of numerical calculations. Having specified Φ, the governing equations become a family of the time evolution equations involving three parameters De, de, and K. It is in these three parameters where we express in our model the individual features of the solvent and the consideration. The

first, De, called a w-Deborah number, arises in the equation governing the time evolution of the solvent mass flux w. It can also be expressed in term of the diffusion Mach number M_{diff} (see (6.29)). The second, de, called a m-Deborah number, appears in the equation governing the time evolution of the internal structure characterized by m. The third one, K, is an indicator of the coupling between diffusion and the internal structure. It measures the relative importance of two contributions to the free energy: the mixing part and the elastic part . The ratio K/De indicates thus the importance of the coupling between diffusion and the structural changes in the polymer. This coupling becomes significant when K/De is large. The three dimensional space with coordinates (De, de, K) is called a parameter space and is denoted by the symbol $\wp$. The correspondence between regions in $\wp$ and types of diffusion is established by utilizing analytical as well as numerical methods. The results of calculations that have been compared with experimental results reported in [Thomas et al. (1978)] are predictions concerning the polymer weight gain and the swelling in one-dimensional sorption. We have identified (see Table 6.1) the three parameters (De, de, K) (i.e. a point in the parameter space $\wp$) characterizing the mixture methanol-poly(methyl methacrylate) observed in [Thomas et al. (1978)]. Our theoretical predictions are found to follow very closely the measured values. We calculate also quantities that have not been directly measured. They are the velocity profiles, internal deformations expressed in the conformation tensor m, and the internal stresses created in the polymer during the diffusion and the swelling.

It is useful to illustrate the difference between the modeling presented in this paper and the classical Case II modeling by comparing these two types of theoretical analysis in the specific context of the experimental observations reported in [Thomas et al (1978)]. Let us recall first the classical Case II analysis. What is the input of the classical Case II modeling? In other words, what are the constitutive relations needed in its governing equations? They are two functions D(c) and η(c) expressing the diffusion coefficient and the longitudinal viscosity coefficient as functions of the solvent concentration c. The output of the classical Case II modeling is the weight gain of the polymer, the swelling, and the extra stress. It has been found that in order to arrive at the output that agrees with

the observed Case II diffusion, the input functions D(c) and η(c) have to involve high jumps (the decrease of the viscosity and the increase of the diffusion coefficient). A natural (and probably the only) interpretation of such jumps is as an expression of the glass-rubber transition. The Case II modeling thus begins with an imposition of the glass-rubber transition. The problem is that this type of transition is not observed in [Thomas et al (1978)].

Now, let us recall what we have done to reproduce the experimental results of Thomas et al. The constitutive relations needed in our governing equations (i.e. the input of our theoretical analysis) are summarized in Table 6.1. What we need are three constants for the diffusion at the surface and other three constants for the diffusion in the core. We emphasize that our input involves constants, not functions. In particular, our constitutive equations do not make any reference to glass-rubber transitions. The output of our theoretical consideration consists of the output of classical Case II models and, in addition to it, properties of the wave propagation, velocity profiles, internal deformations, and the viscosity coefficient as a function of the solvent concentration (see Figures 6.11 and 6.13). We thus note that a part of our output, namely η(c), is an input of the classical Case II modeling. We can compare them. From Figure 6.14 we see that the viscosity indeed decreases with the solvent concentration but the decrease is much smaller than the one introduced as an input of the Case II modeling. In particular, the calculated decrease of the viscosity does not indicate (and this is in agreement with experimental observations reported in Thomas et al.(1978)]) any glass-rubber transition.

Summing up, we conclude that (c,w,m)-model of the mass transport in polymers has a wide range of applicability, it encompasses many previously known models, and is relatively simple from the mathematical point of view. Preliminary investigations also indicate that the model can be relatively easily extended to address an important problem, both from the practical and the fundamental point of view, of diffusion of multicomponent solvents in a multilayer polymeric medium.

Table 6.1. Methanol-PMMA properties used for numerical calculations for Case II

Parameters	surface	core
Equilibrium concentration c_{eq}	0.21	0.21
Equilbrium volume fraction ϕ_{eq}	0.24	0.24
Elastic modulus Go [Pa]	$3.3 .10^{9}$	$3.3 .10^{9}$
diffusion mach number M_{diff}	3.35	6.9
Viscosity [Pa. s]	10^{12}	10^{12}
Diffusivity coefficient [m^2/s]	910^{-13}	910^{-13}
Solvent molar volume [m^3/mol]	$4.05\ 10^{-5}$	$4.05\ 10^{-5}$
Temperature [Kelvin]	297	297
(k, n, g)	(0, 0, 0)	(0, 0, 0)
Film half-thickness L_o [m]	0.210^{-6}	$0.5\ 10^{-3}$
$\tilde{R}_o$ for FENEP model	1, 1.5, 2, 3.5, 5,15	1, 1.5, 2, 3.5, 5,15
Interaction parameter χ	1.15	1.15
K	27.06	27.06
Viscoelastic Deborah number de	0.0118	0.0011

6.8 References

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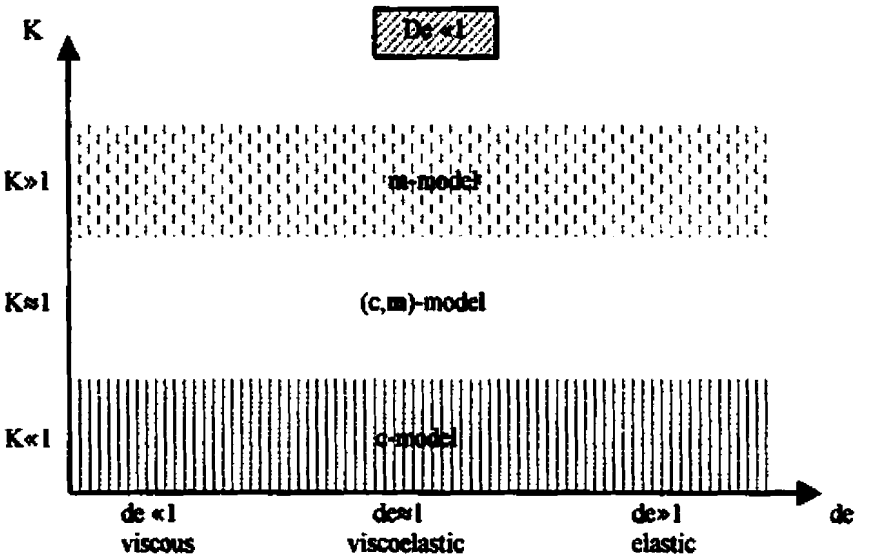

Figure 6.1 K versus de for De<<1. K is the diffusion-internal structure coupling constant, de is m-Deborah number and De is w-Deborah number

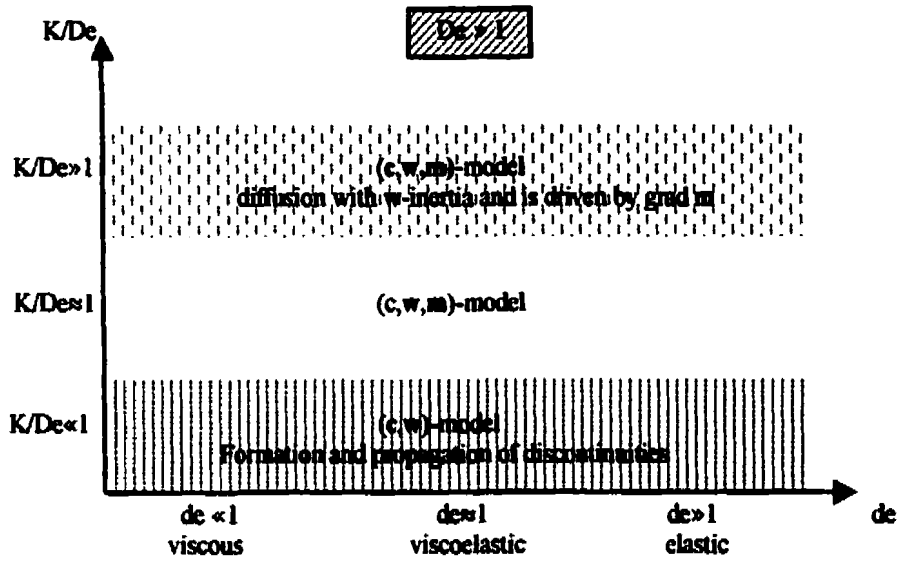

Figure 6.2 K versus de for De>>1. K is the diffusion-internal structure coupling constant, de is m-Deborah number and De is w-Deborah number.

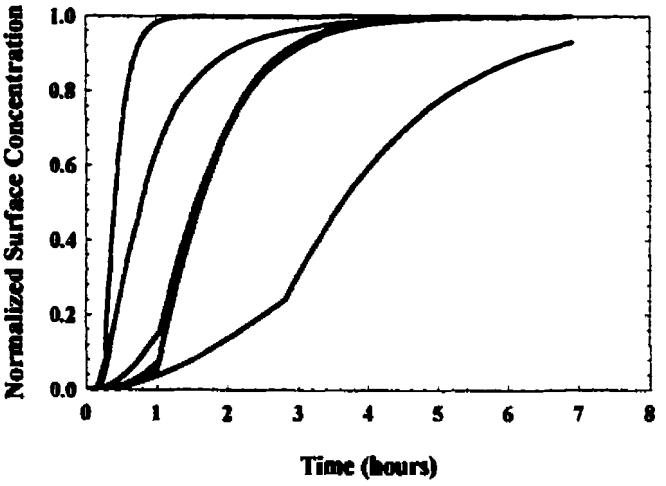

Figure 6.3 Normalized surface concentration profiles versus time (in hours) calculated for k=0, n=0 and g=0. The profiles are shown from left to right for (Ms, Mc) = (1,1), (3.35,1), (3.35,3.35), (3.35,6.9), and (6.9,6.9) respectively.

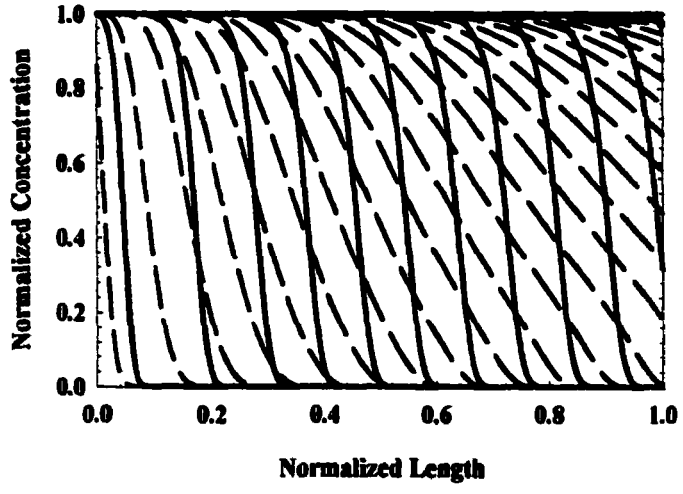

Figure 6.4 Normalized concentration profiles versus normalized length calculated for k=0, n=0 and g=0 and for (Ms, Mc)= (3.35, 6.9) (continuous lines) and for (Ms, Mc)= (6.9, 6.9) (circles). The profiles are shown every 0.1 normalized time step.

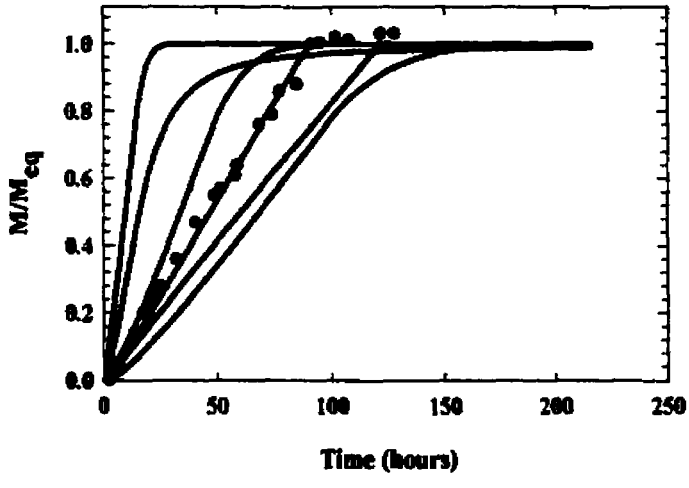

Figure 6.5 Normalized weight gain versus time (in hours) for the parameter k=0, n=0 and g=0. The curves are shown, from left to right, for the following values of (Ms, Mc) = (1,1), (3.35,1), (3.35,3.35), (3.35,6.9), (3.35,20) and (6.9,6.9). The curve in (•) represents the experimental data for methanol-PMMA [Thomas et al. (1978)].

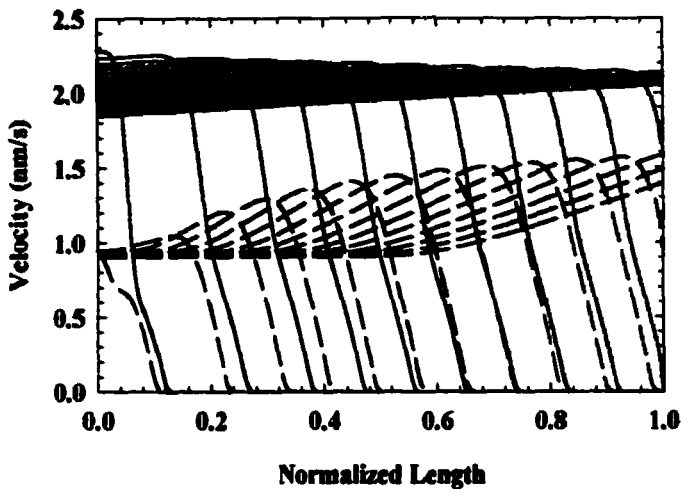

Figure 6.6 Velocity profiles (in nm/sec) versus normalized length calculated for k=0, n=0 and g=0 and for (Ms, Mc)= (3.35, 6.9) (continuous lines) and for (Ms, Mc)= (6.9, 6.9) (circles). The profiles are shown every 0.15 normalized time step.

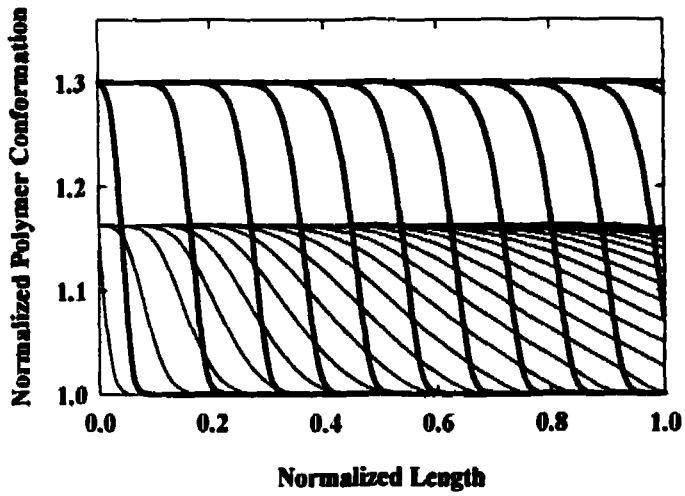

Figure 6.7 Normalized polymer conformation profiles versus normalized length calculated for k=0, n=0 and g=0 and for (Ms, Mc)= (3.35, 6.9) (continuous lines) and for (Ms, Mc)= (6.9, 6.9) (circles). The profiles are shown every 0.1 normalized time step.

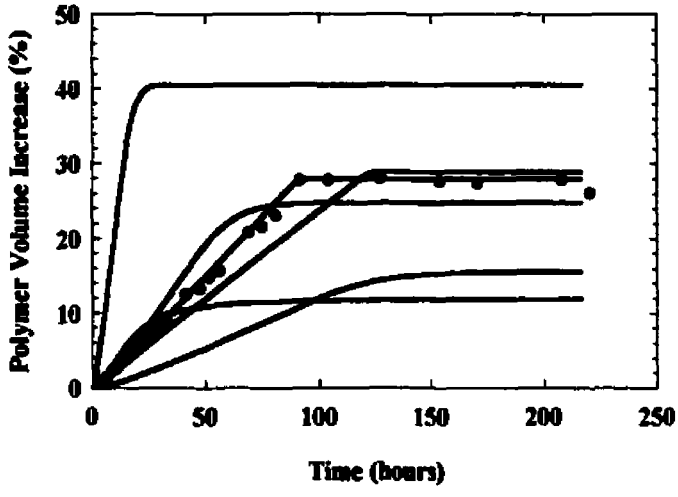

Figure 6.8 Polymer volume increase versus time (in hours) calculated for k=0, n=0 and g=0. The curves are shown for the following values (Ms, Mc) = (1,1), (3.35,20), (3.35,6.9), (3.35,3.35), (6.9,6.9), and (3.35,1) (respectively from top to bottom). The curve in (•) represents the experimental data for methanol-PMMA [Thomas et al. (1978)].

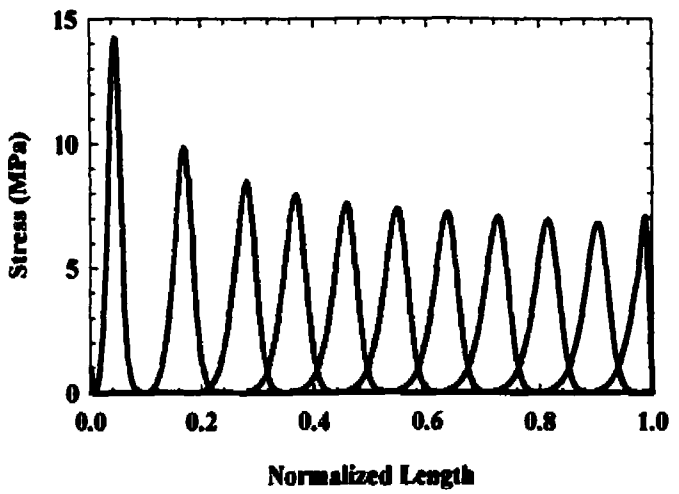

Figure 6.9 Stresses (in MPa) versus normalized length calculated for (k=0, n=0, g=0) and for (Ms, Mc)= (3.35, 6.9). The profiles are shown every 0.1 normalized time step.

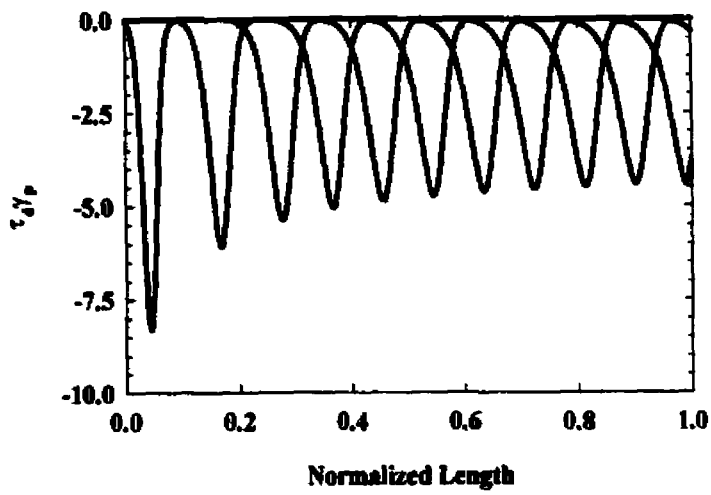

Figure 6.10 Profiles of the gradient of the normalized polymer velocity versus normalized length calculated for (k=0, n=0, g=0) and for (Ms, Mc)= (3.35, 6.9). The profiles are shown every 0.1 normalized time step.

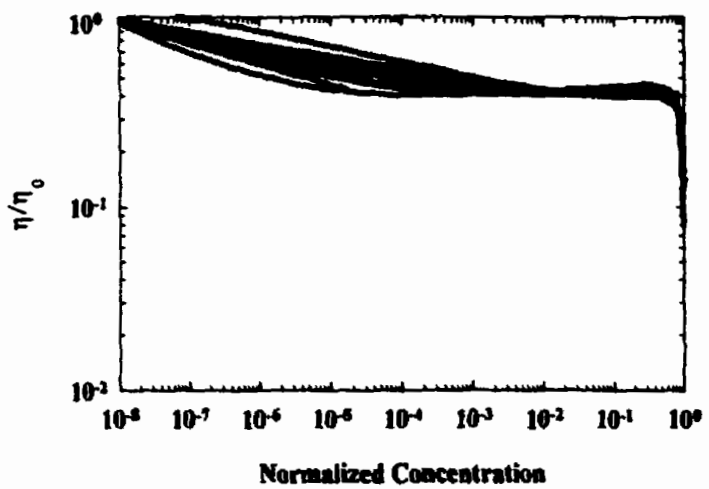

Figure 6.11 Normalized internal viscosity profiles versus normalized concentration calculated using the Maxwell free energy model. The parameters used are (k=0, n=0, g=0) and (Ms, Mc)=(3.35, 6.9).

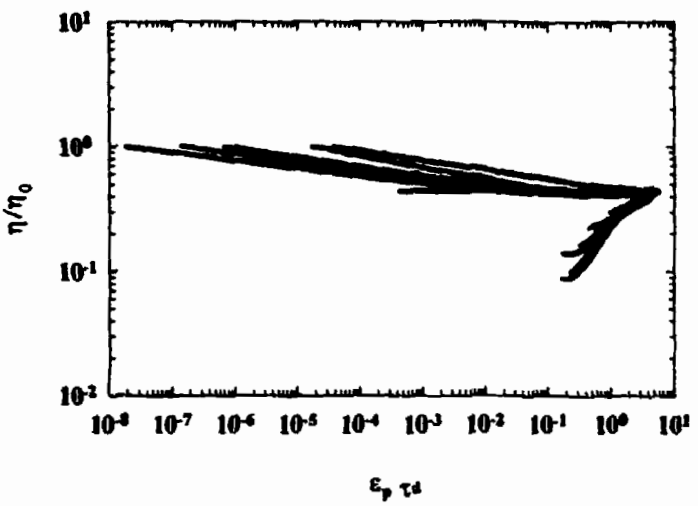

Figure 6.12 Normalized viscosity profiles versus (- normalized polymer velocity gradient) calculated using the Maxwell viscoelastic model. The parameters used are (k=0, n=0, g=0) and (Ms, Mc)=(3.35, 6.9).

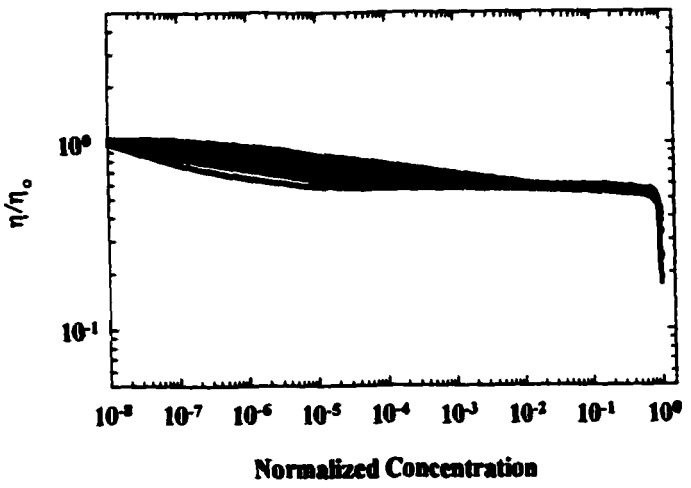

Figure 6.13 Normalized viscosity profiles versus normalized concentration calculated using the FENEP viscoelastic model with $\tilde{R}_o$=2. The parameters used are (k=0, n=0, g=0) and (Ms, Mc)=(3.35, 6.9).

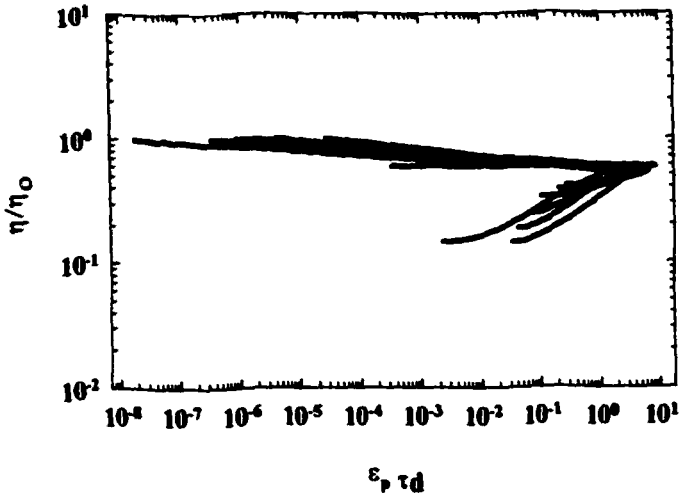

Figure 6.14 Normalized viscosity profiles versus (- normalized polymer velocity gradient) calculated using the FENEP viscoelastic model with $\tilde{R}_o$=2. The parameters used are (k=0, n=0, g=0) and (Ms, Mc)=(3.35, 6.9).

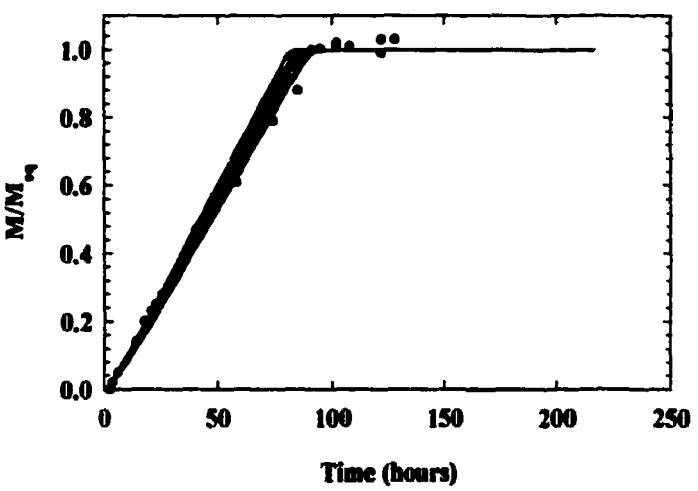

Figure 6.15 Normalized weight gain versus time (in hours)) calculated using the FENEP viscoelastic model for the parameter k=0, n=0 and g=0 and for (Ms, Mc)=(3.35, 6.9). The curves are shown for the following values $\tilde{R}_o$ =1, 1.5, 2, 3.5 (respectively from left to right). The curve in (•) represents the experimental data obtained for methanol-PMMA [Thomas et al. (1978)].

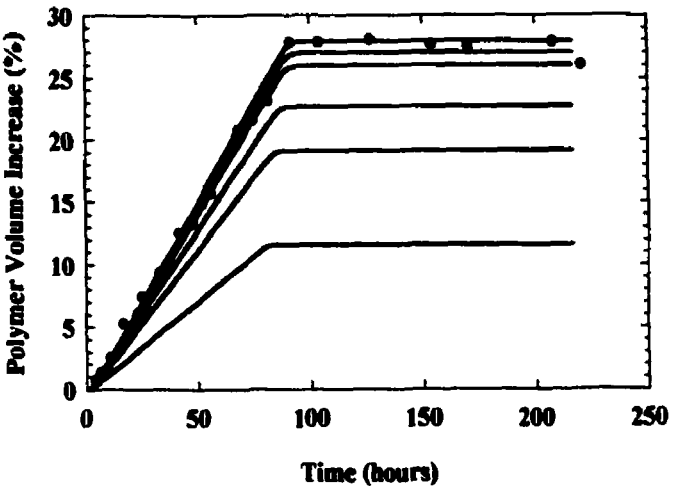

Figure 6.16 Polymer volume increase versus time (in hours) calculated using the FENEP viscoelastic model for k=0, n=0 and g=0 and for (Ms, Mc)=(3.35, 6.9). The curves are shown for the following values of $\tilde{R}_o$ =1, 1.5, 2, 3.5, 5 and 15 (respectively from bottom to top). The curve in (•) represents the experimental data for methanol-PMMA [Thomas et al. (1978)].

CHAPITRE 7

MIXTURE OF TWO SIMPLE AND ONE COMPLEX FLUIDS: I. DIFFUSION and RHEOLOGY

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7.1 Abstract

This paper addresses the coupling among the flow behavior, the diffusion processes and deformations of the internal structure that arise in ternary mixtures consisting of two simple and one complex fluids. States of the mixture are chosen to be described by the fields of the overall mass density, the overall momentum, the mass fractions and of the two simple fluids, two relative momenta, and a second order symmetric tensor characterizing deformations of the internal structure. The model extends to ternary mixtures the model developed previously for binary mixtures consisting one simple and one complex fluids. The governing equations are derived as a particular realization of GENERIC expressing the mathematical structure of the governing equations that guarantees agreement of their solutions with equilibrium thermodynamics. More detailed properties of solutions of the governing equations are investigated in particular situations in which some of the independent state variables become dependent state variables and in both linear and nonlinear regimes. In the nonlinear regime, the overall flow is found to influence the diffusion by making the matrices of the transport coefficients to depend explicitly on the gradient of the overall velocity. This dependence then renders the diffusion highly anisotropic even in the absence of the stresses arising due to deformations of the internal structure. On the other hand, the diffusion process is found to influence the rheological behavior of the mixture by introducing two types of additional stresses: (i) the stresses that arise due to deformations of the internal structure of the complex fluid induced by the diffusion, and (ii) the stresses that are directly expressed in terms of the diffusion fluxes.

7.2 INTRODUCTION

Coupling between rheology and diffusion in a mixture of one solvent and one polymer has been extensively studied both experimentally [1-8] and theoretically [9-20]. Phase separation, swelling, migration across streamlines, formation of morphologies etc. are some of the observed effects that are induced by the applied flow in binary solutions. The two-fluid model has been used [21-22] in many theoretical developments that contributed to understanding such flow-induced behaviors. The application of the flow causes the diffusion to deviate form the predictions of the standard Fick's laws of mass transport. In addition, changes in the polymer structure produced by the diffusion and by the diffusion-rheology coupling create additional stresses within the polymer and thus the observed rheological as well as the internal physical properties are modified. Still new phenomena arise [23-29] in multi-component mixtures due to the cross-coupling of diffusion fluxes of the components.

While engineering applications (separation, drug delivery, drying, coating, etc.) show the tendency towards the use of multi component mixtures, their theoretical investigation has not received enough attention. A notable exception is the thermodynamic-hydrodynamic investigation[30-31] of gels in binary solvents in the absence of viscoelastic deformations. Our objective in this paper is to provide a thermodynamically consistent setting that is suitable for discussing ternary mixtures consisting of two simple fluids (e.g. two solvents) and one complex fluid (e.g. a polymeric fluid). We use the GENERIC [32-33] formalism and extend (in Section 7.3) the two-fluid model [21-22] to a three-fluid model. In the third section, we investigate systematically the coupling between rheology and diffusion for two particular situations: i) the linear regime, and ii) the nonlinear regime. In the former situation (the gradient $\kappa_{\alpha\beta} = \partial v_\beta / \partial r_\alpha$ of the overall velocity v is small), we extend to ternary mixtures the models derived previously for binary mixtures in which the rheology-diffusion couplings play a significant role in both Fickian and non-Fickian regimes. The transport

coefficients are shown, in this case, to be independent of $\kappa_{\alpha\beta}$. In the nonlinear regime, we find that the imposed overall flow causes a flow-induced anisotropy in the diffusion behavior : the transport coefficients become explicit functions of the rate of deformation $\kappa_{\alpha\beta}$.

7.3. MODEL DERIVATION

In this section, we shall derive equations governing the time evolution of a mixture composed of two simple fluids (two solvents) and one complex fluid (polymer). We shall follow GENERIC method. We begin therefore by recalling its physical basis and its mathematical formulation. We continue then by developing its realization representing the three-fluid mixture.

7.3.1 GENERIC Formalism

The modeling developed in classical hydrodynamics proceeds in two stages. In the first stage one chooses a family of experimental observations and looks for a structure of the governing equations that guarantees agreement between the model predictions and the chosen observations. The selected family of experimental observations consists of the conservation of the total mass, momentum and energy, and the compatibility with thermodynamics (i.e. the observation according to which externally unforced systems are seen to reach eventually states at which their behavior is seen to be well described by equilibrium thermodynamics). In the second stage, a particular realization of the structure identified in the first stage is found. The realization (also called a constitutive relation) reflects the particular nature of the fluid under consideration.

Classical hydrodynamics considers only simple fluids whose states are completely and universally described by classical hydrodynamic fields. The structure identified in the first stage is the structure of local conservation laws (derivative with respect to time

equals divergence of a flux). Fluids are called complex if the classical hydrodynamic fields do not suffice to describe their states. If we thus want to follow the two-stage modeling developed in classical hydrodynamics also in the context of complex fluids we have to find in the first stage a new structure that can be applied also for general state variables. Such structure is called GENERIC (General Equation for Non-Equilibrium Reversible-Irreversible Coupling) [32-33]. In the rest of this subsection, we shall recall its mathematical formulation. The second stage, a search for its realization expressing the three-fluid mixture under consideration, is presented in Subsections 7.3-7.6.

We shall assume in this paper that the system under consideration is kept under constant temperature denoted by the symbol T. Let x be the set of state variables. The time evolution of x, that is guaranteed to agree with the observed conservation of the total mass, momentum, energy, and with thermodynamics , is governed by

$$\frac{\partial x}{\partial t} = L\frac{\delta \Phi}{\delta x} - \frac{\delta \Psi}{\delta(\delta\Phi/\delta x)} \tag{7.1}$$

We shall now explain the meanings of the symbols introduced in (7.1). By t we denote the time. Φ is the Helmholtz free energy, $\Phi = E - TS + \mu N$, E , S and N are respectively the global energy, the global entropy, and the global number of moles of the system; μ the chemical potential; $\frac{\delta\Phi}{\delta x}$ is the conjugate variable of x ($\delta/\delta x$ denotes the functional derivative). By the symbol L we denote the Poisson bi-vector and $\Psi(\delta\Phi/\delta x)$ is a dissipation potential. The GENERIC equation introduced in previous works [32-33] reduces to (1) since the temperature is assumed to be kept constant during the whole process of the evolution [34].

We say that L is a Poisson bivector if the following is satisfied: Let A and B be real valued functions of x. We construct a bracket $\{A,B\} = \left\langle \frac{\delta A}{\delta x}, L\frac{\delta B}{\delta x} \right\rangle$ where < , > is the

inner product. This bracket is called a Poisson bracket if (i) $\{A,B\}=-\{B,A\}$ (this means that L is a skew symmetric matrix, i.e. $L_{ij}=-L_{ji}$), (ii) the Jacobi identity $\{\{B,C\}A\}+\{\{A,B\}C\}+\{\{C,A\}B\}=0$ holds. We require moreover that the Poisson bivector is degenerate so that $L\frac{\delta S}{\delta x}=0$ and $L\frac{\delta N}{\delta x}=0$. From the physical point of view, the Poisson bivector L expresses the Poisson kinematics of the state variables x.

The dissipation potential Ψ is a real valued function of $\delta\Phi/\delta x$ satisfying the following properties: (i) $\Psi(0)=0$, (ii) Ψ reaches its minimum at 0, (iii) Ψ is a convex in a neighborhood of 0, and (iv) Ψ is degenerate so that $<\frac{\delta E}{\delta x},\frac{\delta\Psi}{\delta(\delta\Phi/\delta x)}>=<\frac{\delta N}{\delta x},\frac{\delta\Psi}{\delta(\delta\Phi/\delta x)}>=0$. A particular example of the dissipation potential that is often used in applications is the following: $\Psi(\frac{\delta A}{\delta x})=\left(\frac{\delta A}{\delta x},M\frac{\delta A}{\delta x}\right)$ where M is a nonnegative symmetric matrix satisfying $M\frac{\delta E}{\delta x}=0$, $M\frac{\delta N}{\delta x}=0$. It is easy to verify that (7.1) implies the conservation of energy ($\frac{dE}{dt}=0$), conservation of number of moles ($\frac{dN}{dt}=0$), and the dissipation inequality ($\frac{d\Phi}{dt}=<\frac{\delta\Phi}{\delta x},L\frac{\delta\Phi}{\delta x}>-<\frac{\delta\Phi}{\delta x},\frac{\delta\Psi}{\delta(\delta\Phi/\delta x)}>\le 0$). Equation (7.1) can also be written as an equation $\frac{dA}{dt}=\{A,\Phi\}-<\frac{\delta A}{\delta x},\frac{\delta\Psi}{\delta(\delta\Phi/\delta x)}>$ that is required to hold for all sufficiently regular real valued functions A.

A particular realization of (7.1) consists of the following four steps: (i) specification of the state variables x, (ii) specification of their Poisson kinematics (i.e. specification of L), (iii) specification of the dissipative structure (i.e. specification of the dissipation potential Ψ), (iv) specification of the Helmholtz free energy Φ. These four steps are made in the following subsections.

7.3.2 State Variables

The system that we consider consists of two simple fluids (e.g. solvents) and one complex fluid (e.g. polymer). Each component composing the mixture is characterized, on the hydrodynamics-type level of description that we adopt, by its mass density ρ_i and by its momentum density $\mathbf{u}_i$ (i=1,2 for the two simple fluids and i = p for the polymer). In addition, the internal structure of the complex fluid component is chosen to be characterized by either the configuration space distribution function $\psi(t, \mathbf{r}, \mathbf{R})$ [35] (t is time, $\mathbf{r}$ is the position vector and $\mathbf{R}$ is the end-to-end vector of the polymeric chain) or its second moment $\mathbf{m}$, called a conformation tensor (a second order symmetric and positive definite tensor).

Following the viewpoint that we used in the two-fluid models [18], the mixture is regarded in the three-fluid model as a system whose set of state variables x is given by

$$x = (\rho_1, \mathbf{u}_1, \rho_2, \mathbf{u}_2, \rho_p, \mathbf{u}_p, \psi) \tag{7.2}$$

if ψ is used to characterized the internal structure of the polymeric component, or by

$$x = (\rho_1, \mathbf{u}_1, \rho_2, \mathbf{u}_2, \rho_p, \mathbf{u}_p, \mathbf{m}) \tag{7.3}$$

if $\mathbf{m}$ characterizes the internal structure of the polymeric component. As in the two-fluid model, we introduce new coordinates in the space of state variables by

$$\rho = \rho_1 + \rho_2 + \rho_p$$

$$\mathbf{u} = \mathbf{u}_1 + \mathbf{u}_2 + \mathbf{u}_p$$

$$c_1 = \frac{\rho_1}{\rho_1 + \rho_2 + \rho_p}$$

$$c_2 = \frac{\rho_2}{\rho_1 + \rho_2 + \rho_p} \tag{7.4}$$

$$\mathbf{w}_1 = \left(1 - \frac{\rho_1}{\rho}\right)\mathbf{u}_1 - \frac{\rho_1}{\rho}\mathbf{u}_2 - \frac{\rho_1}{\rho}\mathbf{u}_p$$

$$\mathbf{w}_2 = \left(1 - \frac{\rho_2}{\rho}\right)\mathbf{u}_2 - \frac{\rho_2}{\rho}\mathbf{u}_1 - \frac{\rho_2}{\rho}\mathbf{u}_p$$

where ρ is the overall mass density, $\mathbf{u}$ is the overall momentum density, c_i is the mass fractions of the i-th component and $\mathbf{w}_i$ stands for its relative momentum density [36]. We will show in the forthcoming section that the relative momentum density defined above coincides exactly with the mass flux density relative to the local mass-average velocity [37-38]. The transformation (7.4) is completed by

$$\mathbf{w}_1 + \mathbf{w}_2 + \mathbf{w}_p = 0 \tag{7.5}$$

where $\mathbf{w}_p$ designates the relative momentum density of the polymer. The set of the state variables becomes, under the transformation (7.4),

$$x = (\rho, \mathbf{u}, c_1, \mathbf{w}_1, c_2, \mathbf{w}_2, \psi) \tag{7.6}$$

or

$$x = (\rho, \mathbf{u}, c_1, \mathbf{w}_2, c_2, \mathbf{w}_2, \mathbf{m}) \tag{7.7}$$

which correspond respectively to the expressions (7.2) and (7.3). In the following, we aim at deriving the Poisson kinematics of the state variables (7.6) and (7.7).

7.3.3 Poisson Kinematics

The nondissipative (Poisson) structure which constitutes the second step of the GENERIC algorithm is embodied in the Poisson bivector L. For convenience, we write the Poisson bracket for the sets of state variables (7.6) and (7.7) as a sum of two contributions

$$\{A,B\} = \{A,B\}^{(cfm)} + \{A,B\}^{(is)} \tag{7.8}$$

The superscript (cfm) designates classical fluid mechanics and the superscript (is) stands for internal structure. The first term on the right hand side expresses the (Poisson) structure of the three components (regarded as simple fluids) and the second term on the right hand side expresses the Poisson structure expressing kinematics of the internal structure of the third component;

$$\{A,B\}^{(\text{cm})} = \int d\mathbf{r}\,\Big[\rho\partial_\alpha\big(A_\rho\big)B_{u_\alpha} + u_\gamma\partial_\alpha\big(A_{u_\gamma}\big)B_{u_\alpha} - A_{c_1}B_{u_\alpha}\partial_\alpha c_1 - A_{c_2}B_{u_\alpha}\partial_\alpha c_2$$
$$-\rho c_1c_2\partial_\alpha\left(\frac{A_{c_1}}{\rho}\right)B_{w_{2\alpha}} + \rho c_2(1-c_2)\partial_\alpha\left(\frac{A_{c_2}}{\rho}\right)B_{w_{2\alpha}} - \rho c_1c_2\partial_\alpha\left(\frac{A_{c_2}}{\rho}\right)B_{w_{1\alpha}}$$
$$+\rho c_1(1-c_1)\partial_\alpha\left(\frac{A_{c_1}}{\rho}\right)B_{w_{1\alpha}} + w_{1\gamma}\partial_\alpha\big(A_{u_\gamma}\big)B_{w_{1\alpha}} + w_{2\alpha}\partial_\alpha\big(A_{u_\gamma}\big)B_{w_{2\alpha}}$$
$$-\rho c_1(1-c_1)\partial_\alpha\left(\frac{u_\gamma}{\rho}A_{w_{1\gamma}}\right)B_{w_{1\alpha}} + \rho c_1c_2\partial_\alpha\left(\frac{u_\gamma}{\rho}A_{w_{1\gamma}}\right)B_{w_{2\alpha}} - w_{1\gamma}A_{w_{1\gamma}}B_{w_{1\gamma}}\partial_\alpha c_1$$
$$-(1-2c_1)w_{1\gamma}\partial_\alpha\big(A_{w_{1\gamma}}\big)B_{w_{1\alpha}} + w_{1\gamma}\partial_\alpha\big(A_{w_{1\gamma}}\big)B_{u_\alpha} - w_{2\gamma}\partial_\alpha\big(c_1A_{w_{1\gamma}}\big)B_{w_{2\alpha}}$$
$$+c_1(1-c_1)u_\gamma\partial_\alpha\big(A_{w_{1\gamma}}\big)B_{w_{1\alpha}} - c_1c_2u_\gamma\partial_\alpha\big(A_{w_{1\gamma}}\big)B_{w_{2\gamma}} - c_2w_{1\gamma}\partial_\alpha\big(A_{w_{1\gamma}}\big)B_{w_{2\alpha}}$$
$$+\rho c_1c_2\partial_\alpha\left(\frac{u_\gamma}{\rho}A_{w_{2\gamma}}\right)B_{w_{1\alpha}} - \rho c_2(1-c_2)\partial_\alpha\left(\frac{u_\gamma}{\rho}A_{w_{2\gamma}}\right)B_{w_{2\alpha}} - w_{1\gamma}\partial_\alpha\big(c_2A_{w_{2\gamma}}\big)B_{w_{1\alpha}}$$
$$-w_{2\gamma}A_{w_{2\gamma}}B_{w_{2\alpha}}\partial_\alpha c_2 - (1-2c_2)w_{2\gamma}\partial_\alpha\big(A_{w_{2\gamma}}\big)B_{w_{2\alpha}} + w_{2\gamma}\partial_\alpha\big(A_{w_{2\gamma}}\big)B_{u_\alpha}$$
$$-c_1c_2u_\gamma\partial_\alpha\big(A_{w_{2\gamma}}\big)B_{w_{1\alpha}} - c_1w_{2\gamma}\partial_\alpha\big(A_{w_{2\gamma}}\big)B_{w_{1\alpha}} + c_2(1-c_2)u_\gamma\,\partial_\alpha\big(A_{w_{2\gamma}}\big)B_{w_{2\alpha}}$$
$$-\quad A\leftrightarrow B\ \Big] \tag{7.9}$$

$X_\alpha := \delta X/\delta a$, where $X = A, B$; u_i is the i-th component of the vector variable $\mathbf{u}$, etc., $A \leftrightarrow B$ represents the same as above but with A and B interchanged. The internal-structure contribution to the Poisson bracket is

$$\{A,B\}^{(\text{in})} = \int d\mathbf{r}\int d\mathbf{R}\,\Big[\psi\partial_\gamma\big(A_\psi\big)B_{u_\gamma} - c_1\psi\partial_\gamma\big(A_\psi\big)B_{w_{1\gamma}} - c_2\psi\partial_\gamma\big(A_\psi\big)B_{w_{2\gamma}}$$
$$+\psi R_\beta\frac{\partial}{\partial R_\gamma}\big(A_\psi\big)\partial_\beta B_{u_\gamma} - \psi R_\beta\frac{\partial}{\partial R_\gamma}\big(A_\psi\big)\partial_\beta\big(c_1B_{w_{1\gamma}}\big)$$
$$-\psi R_\beta\frac{\partial}{\partial R_\gamma}\big(A_\psi\big)\partial_\beta\big(c_2B_{w_{2\gamma}}\big) - \quad A\leftrightarrow B\Big] \tag{7.10}$$

if ψ is used to characterize the internal structure, and

$$\{A,B\}^{(is)} = \int dr \Big[m_{\alpha\beta}\partial_\gamma\left(A_{m_{\alpha\beta}}\right)B_{u_\gamma} - c_1 m_{\alpha\beta}\partial_\gamma\left(A_{m_{\alpha\beta}}\right)B_{w_{1\gamma}} - c_2 m_{\alpha\chi}\partial_\gamma\left(A_{m_{\alpha\beta}}\right)B_{w_{2\gamma}}$$
$$+ m_{\gamma\alpha}A_{m_{\alpha\beta}}\partial_\gamma B_{u_\beta} - m_{\gamma\alpha}A_{m_{\alpha\beta}}\partial_\beta\left(c_1 B_{w_{1\gamma}}\right)$$
$$- m_{\gamma\alpha}A_{m_{\alpha\beta}}\partial_\beta\left(c_2 B_{w_{2\gamma}}\right) + m_{\gamma\beta}A_{m_{\alpha\beta}}\partial_\gamma B_{u_\alpha} - m_{\gamma\beta}A_{m_{\alpha\beta}}\partial_\gamma\left(c_1 B_{w_{1\alpha}}\right)$$
$$- m_{\gamma\beta}A_{m_{\alpha\beta}}\partial_\gamma\left(c_2 B_{w_{2\alpha}}\right) - \quad A \leftrightarrow B\Big] \tag{7.11}$$

if $\mathbf{m}$ is chosen as the internal state variable. The brackets (7.8)-(7.11) are derived in the same way as the similar brackets have been derived in the context of the two-fluid model in [18]. We briefly recall the derivation. We begin by writing the well known Poisson brackets for the state variables $(\rho_1,\mathbf{u}_1)$, $(\rho_2,\mathbf{u}_2)$ and $(\rho_p,\mathbf{u}_p)$ [39] and for the state variables ψ and $\mathbf{m}$ [40]. To obtain then the Poisson bracket (7.9), we use the one-to-one transformation (7.4) and the fact that under a one-to-one transformation a Poisson bracket transforms into another Poisson bracket.

7.3.4. Dissipative Kinematics

Each solvent, a structureless fluid, contributes to the dissipation phenomena by its own matrix of viscosity coefficients representing its response to the overall and relative motions. The polymer is a complex fluid whose mechanical deformations are viscoelastic. The relative momenta $\mathbf{w}_1$ and $\mathbf{w}_2$ are not conserved, their dissipation involves a drag term accounting for the relaxation produced by the friction between the components.

Similarly as we did in the presentation of the Poisson structure (see (7.8)) we write the dissipation potential as a sum of two potentials

$$\Psi = \Psi^{(cfm)} + \Psi^{(is)} \tag{7.12}$$

where

$$\Psi^{(cfm)}(A_{x_e}) = \int dr \tfrac{1}{2}\left(\nabla_{x_e} A\right)^T \eta \left(\nabla_{x_e} A\right) + \int dr \tfrac{1}{2}\left(\nabla^b_{x_e} A\right)^T \eta_b \left(\nabla^b_{x_e} A\right) + \int dr (A_w)^T \frac{\Lambda}{2}(A_w) \tag{7.13}$$

we have used the notation: $x_e = (u, \quad w_1, \quad w_2)^T$.

The internal structure contribution is

$$\Psi^{(is)}(A_\psi) = \int d\mathbf{R} \left(\frac{\partial A_\psi}{\partial R_\alpha}\right) \frac{\Gamma}{2} \left(\frac{\partial A_\psi}{\partial R_\alpha}\right) \tag{7.14}$$

if (7.6) serves as state variables and

$$\Psi^{(is)}(A_m) = \int dr \, A_{m_{\alpha\beta}} m_{\beta\theta} m_{\theta\gamma} \lambda \, A_{m_{\gamma\varepsilon}} \tag{7.15}$$

if (7.7) serves as state variables. In (7.13)-(7.15), we use the following notation:

$$\nabla_{x_e} A = \left(\partial_\alpha A_{u_\beta} + \partial_\beta A_{u_\alpha}, \partial_\alpha A_{w_{1\beta}} + \partial_\beta A_{w_{1\alpha}}, \partial_\alpha A_{w_{2\beta}} + \partial_\beta A_{w_{2\alpha}}\right)^T \tag{7.16}$$

$$\nabla^b_{x_e} A = \left(\partial_\alpha A_{u_\alpha}, \partial_\alpha A_{w_{1\alpha}}, \partial_\alpha A_{w_{2\alpha}}\right)^T \tag{7.17}$$

$$A_w = \left(A_{w_1}, A_{w_2}\right) \tag{7.18}$$

$$\eta = \begin{pmatrix} \eta & \nu_{12} & \nu_{13} \\ \nu_{21} & \eta_1^r & \nu_{23} \\ \nu_{31} & \nu_{32} & \eta_2^r \end{pmatrix} \tag{7.19}$$

$$\eta_b = \begin{pmatrix} \eta_b & \nu_{b12} & \nu_{b13} \\ \nu_{b21} & \eta^r_{b1} & \nu_{b23} \\ \nu_{b31} & \nu_{b32} & \eta^r_{b2} \end{pmatrix} \tag{7.20}$$

and

$$\Lambda = \begin{pmatrix} \Lambda_1 & \Lambda_{12} \\ \Lambda_{21} & \Lambda_2 \end{pmatrix} \tag{7.21}$$

The superscript or subscript "b" stands for "bulk". It is easily seen that the dissipation potential (7.12) satisfies the properties listed in Section 7.3.1 if (7.19), (7.20), (7.21) are symmetric and positive definite matrices and Γ and λ are positive. The physical interpretation of these quantities will be discussed in the context of the governing equations in the following subsection.

7.3.5 Evolution Equations

By inserting the above Poisson bracket and dissipation potential into (7.1) we obtain:

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha \left(\rho \Phi_{u_\alpha}\right)$$

$$\frac{\partial u_\gamma}{\partial t} = -\partial_\alpha \left(u_\gamma \Phi_{u_\alpha}\right) - \partial_\gamma p - \partial_\alpha \sigma_{\alpha\gamma}$$

$$\rho \frac{\partial c_1}{\partial t} = -\rho \Phi_{u_\alpha} \partial_\alpha c_1 - \partial_\alpha \left(\rho c_1 (1 - c_1) \Phi_{w_{1\alpha}} - \rho c_1 c_2 \Phi_{w_{2\alpha}}\right)$$

$$\rho \frac{\partial c_2}{\partial t} = -\rho \Phi_{u_\alpha} \partial_\alpha c_2 - \partial_\alpha \left(\rho c_2 (1 - c_2) \Phi_{w_{2\alpha}} - \rho c_1 c_2 \Phi_{w_{1\alpha}}\right)$$

$$\frac{\partial w_{1\gamma}}{\partial t} = -\partial_\alpha\left(w_{1\gamma}\Phi_{u_\alpha}\right) - w_{1\alpha}\partial_\gamma\left(\Phi_{u_\alpha}\right) - \rho c_1(1-c_1)\partial_\gamma\left(\frac{\Phi_{c_1}}{\rho}\right) + \rho c_1 c_2\partial_\gamma\left(\frac{\Phi_{c_2}}{\rho}\right)$$
$$-(1-2c_1)\left[\partial_\alpha\left(w_{1\gamma}\Phi_{w_{1\alpha}}\right) + w_{1\alpha}\partial_\gamma\Phi_{w_{1\alpha}}\right] + w_{1\gamma}\Phi_{w_{1\alpha}}\partial_\alpha c_1 + w_{1\alpha}\Phi_{w_{1\alpha}}\partial_\gamma c_1$$
$$+ w_{1\alpha}\partial_\gamma\left(c_2\Phi_{w_{2\alpha}}\right) + c_1 w_{2\alpha}\partial_\gamma\Phi_{w_{2\alpha}} + \partial_\alpha\left(c_2 w_{1\gamma}\Phi_{w_{2\alpha}}\right) + c_1\partial_\alpha\left(w_{2\gamma}\Phi_{w_{2\alpha}}\right)$$
$$+\left(\rho c_1(1-c_1)\Phi_{w_{1\alpha}} - \rho c_1 c_2\Phi_{w_{2\alpha}}\right)\omega_{\gamma\alpha} + \left(\frac{\partial w_{1\gamma}}{\partial t}\right)^{(is)}$$
$$-\partial_\alpha\sigma^{1r}_{\alpha\gamma} - \Lambda_1\Phi_{w_{1\gamma}} - \Lambda_{12}\Phi_{w_{2\gamma}}$$

$$\frac{\partial w_{2\gamma}}{\partial t} = -\partial_\alpha\left(w_{2\gamma}\Phi_{u_\alpha}\right) - w_{2\alpha}\partial_\gamma\left(\Phi_{u_\alpha}\right) - \rho c_2(1-c_2)\partial_\gamma\left(\frac{\Phi_{c_2}}{\rho}\right) + \rho c_1 c_2\partial_\gamma\left(\frac{\Phi_{c1}}{\rho}\right)$$
$$-(1-2c_2)\left[\partial_\alpha\left(w_{2\gamma}\Phi_{w_{2\alpha}}\right) + w_{2\alpha}\partial_\gamma\Phi_{w_{2\alpha}}\right] + w_{2\gamma}\Phi_{w_{2\alpha}}\partial_\alpha c_2 + w_{2\alpha}\Phi_{w_{2\alpha}}\partial_\gamma c_2$$
$$+ w_{2\alpha}\partial_\gamma\left(c_1\Phi_{w_{1\alpha}}\right) + c_2 w_{1\alpha}\partial_\gamma\Phi_{w_{1\alpha}} + \partial_\alpha\left(c_1 w_{2\gamma}\Phi_{w_{1\alpha}}\right) + c_2\partial_\alpha\left(w_{1\gamma}\Phi_{w_{1\alpha}}\right)$$
$$+\left(\rho c_2(1-c_2)\Phi_{w_{2\alpha}} - \rho c_1 c_2\Phi_{w_{1\alpha}}\right)\omega_{\gamma\alpha} + \left(\frac{\partial w_{2\gamma}}{\partial t}\right)^{(is)}$$
$$-\partial_\alpha\sigma^{2r}_{\alpha\gamma} - \Lambda_2\Phi_{w_{2\gamma}} - \Lambda_{12}\Phi_{w_{1\gamma}}$$

(7.22)

$$\frac{\partial\psi}{\partial t} = -\partial_\gamma\left(\psi\Phi_{u_\gamma}\right) + \partial_\gamma\left(c_1\psi\Phi_{w_{1\gamma}}\right) + \partial_\gamma\left(c_2\psi\Phi_{w_{2\gamma}}\right) - \frac{\partial}{\partial R_\gamma}\left(\psi R_\beta\partial_\beta\Phi_{u_\gamma}\right) + \frac{\partial}{\partial R_\gamma}\left(\psi R_\beta\partial_\beta\left(c_1\Phi_{w_{1\gamma}}\right)\right)$$
$$+\frac{\partial}{\partial R_\gamma}\left(\psi R_\beta\partial_\beta\left(c_2\Phi_{w_{2\gamma}}\right)\right) + \frac{\partial}{\partial R_\alpha}\left(\Gamma\psi\frac{\partial}{\partial R_\alpha}\left(\Phi_\psi\right)\right)$$

(7.23)

if ψ is used as the internal structure state variable and

$$\frac{\partial m_{\alpha\beta}}{\partial t} = -\partial_\gamma\left(m_{\alpha\beta}\Phi_{u_\gamma}\right) + m_{\gamma\alpha}\partial_\gamma\Phi_{u_\beta} + m_{\gamma\beta}\partial_\gamma\Phi_{u_\alpha}$$
$$+\partial_\gamma\left(m_{\alpha\beta}c_1\Phi_{w_{1\gamma}}\right) - m_{\gamma\alpha}\partial_\gamma\left(c_1\Phi_{w_{1\beta}}\right) - m_{\gamma\beta}\partial_\gamma\left(c_1\Phi_{w_{1\alpha}}\right)$$
$$+\partial_\gamma\left(m_{\alpha\beta}c_2\Phi_{w_{2\gamma}}\right) - m_{\gamma\alpha}\partial_\gamma\left(c_2\Phi_{w_{2\beta}}\right) - m_{\gamma\beta}\partial_\gamma\left(c_2\Phi_{w_{2\alpha}}\right) - \lambda m_{\alpha\gamma}\sigma^{(is)}_{\gamma\beta}$$

(7.24)

if $\mathbf{m}$ is used as the internal structure state variable.

In the rest of this section, we shall explain the meaning of the symbols that have not been explained before and comment about the physical meaning of the terms appearing in the above time evolution equations.

The first equation in (7.22) expresses the global mass conservation. Since the free energy Φ involves always the term $\int d\mathbf{r}\left[\frac{\mathbf{u}^2}{2\rho}\right]$, where ρ is the constant overall mass density, (this term is a part of the kinetic energy) then $\Phi_{\mathbf{u}} = \mathbf{v} = \mathbf{u}/\rho$ is the overall velocity.

The second equation expresses the conservation of the overall momentum, p stands for the hydrodynamic pressure given by

$$p = -\tilde{\varphi} + \rho\Phi_{\rho} + u_{\gamma}\Phi_{u_{\gamma}} + w_{1\gamma}\Phi_{w_{1\gamma}} + w_{2\gamma}\Phi_{w_{2\gamma}} + \int d\mathbf{R}\psi\Phi_{\psi} \tag{7.25}$$

if ψ is used as the internal state variable and

$$p = -\tilde{\varphi} + \rho\Phi_{\rho} + u_{\gamma}\Phi_{u_{\gamma}} + w_{1\gamma}\Phi_{w_{1\gamma}} + w_{2\gamma}\Phi_{w_{2\gamma}} + m_{\alpha\beta}\Phi_{m_{\alpha\beta}} \tag{7.26}$$

if $\mathbf{m}$ is used as the internal state variable; $\tilde{\varphi}$ is the density of Φ (i.e. $\Phi = \int d\mathbf{r}\tilde{\varphi}$), and σ is the overall extra stress tensor given by

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(ww)} + \sigma_{\alpha\beta}^{s} - \sigma_{\alpha\beta}^{(ik)} \tag{7.27}$$

where

$$\sigma_{\alpha\beta}^{(ww)} = w_{1\alpha}\Phi_{w_{1\beta}} + w_{2\alpha}\Phi_{w_{2\beta}} \tag{7.28}$$

$$\begin{pmatrix} \sigma^{s} \\ \sigma^{1r} \\ \sigma^{2r} \end{pmatrix} = -\eta \nabla_{x_e} \Phi - \eta_b \nabla^{b}_{x_e} \Phi \tag{7.29}$$

η and η_b are the matrices (7.19), (7.20) , and

$$\sigma^{(is)}_{\alpha\beta} = \int d\mathbf{R}\, R_\beta \psi \frac{\partial}{\partial R_\alpha} \Phi_\psi \tag{7.30}$$

respectively

$$\sigma^{(is)}_{\alpha\beta} = 2 m_{\alpha\gamma} \Phi_{m_{\gamma\beta}} \tag{7.31}$$

if ψ respectively $\mathbf{m}$ is used to describe the internal structure of the polymeric fluid. The first term $\sigma^{(ww)}$ in (7.27), which arises form the Poisson bracket (the reversible part of GENERIC) as a consequence of the use of the three-fluid-model, is the diffusion contribution to the extra stress tensor. Summing up, we see that the second equation in (7.23) couples the flow, the diffusion process and deformations of the internal structure of the complex fluid. Well studied experimentally are the effects of such coupling in binary semi-dilute solutions. It has been revealed [1-8] by both light scattering and rheology experiments that the flow causes the development of structures and stresses after imposing a simple shear to homogeneous solutions. For instance, in the semi-dilute solution of polystyrene (PS) with dioctyl phthlate (DOP), two overshoots were detected in the shear and normal stress values upon imposing a high shear rate [8]. In addition, light scattering measurements for these systems exhibit several interesting features as for example the so-called ' butterfly' pattern [1-8] which has been identified to correspond to the second overshoot and to its time evolution. The physics that is behind these

phenomena has been understood to be mainly due the elastic character of the entangled polymeric chains in the semi-dilute regime. Less investigated is the direct influence of diffusion on the flow. The quadratic stresses $\sigma^{(ww)}$, even if they are generally small (quadratic terms), may bring significant changes to the behavior of the flow particularly in the parameter regions where the fluctuation of the concentration are significantly large. In semi-dilute ternary mixtures, new complex phenomena are expected to occur due to the cross coupling arising among the diffusion fluxes in addition to their coupling to the elastic deformations of the internal structure. Notice that the analogical contribution, $\mathbf{u}\Phi_{\mathbf{u}}$, arising in the momentum balance equation is a part of the stress tensor but does not contribute to the extra stress tensor (see the first term on the right side of the second equation in (7.22)). The second term in (7.27) is the dissipative Navier-Stokes-like term that combines the contributions arising due to gradients of the overall and relative momenta. Moreover, this term is a sum of two parts, one of which stems only from the bulk deformations (the second term on the right hand side of (7.29)). The third contribution to the extra stress tensor arises in the internal structure of the polymeric component.

The third and fourth equations in (7.22) are the equations governing the time evolution of the mass fractions c_1 and c_2. From these equations, we identify the mass fluxes to be:

$$J_{1\alpha} = \rho c_1(1-c_1)\Phi_{w_{1\alpha}} - \rho c_1 c_2 \Phi_{w_{2\alpha}} \tag{7.32}$$

$$J_{2\alpha} = \rho c_2(1-c_2)\Phi_{w_{2\alpha}} - \rho c_1 c_2 \Phi_{w_{1\alpha}} \tag{7.33}$$

or in the matrix form

$$\mathbf{J}_{\alpha} = \mathbf{A}\,\Phi_{w_{\alpha}} \tag{7.34}$$

where

$$\mathbf{A}=\begin{pmatrix}\rho c_1(1-c_1) & -\rho c_1 c_2\\ -\rho c_1 c_2 & \rho c_2(1-c_2)\end{pmatrix} \tag{7.35}$$

and $\mathbf{J}_\alpha=(J_{1\alpha},\ J_{2\alpha})^T$, $\Phi_{w_\alpha}=(\Phi_{w_{1\alpha}},\ \Phi_{w_{2\alpha}})^T$. Note that the matrix **A** is symmetric and that $\det\mathbf{A}=\rho^2c_1c_2c_p\geq 0$ ($c_p=1-c_1-c_2$ is the polymer mass fraction).

The fifth and sixth equations in (7.22) are the equations governing the time evolution of the relative momenta $\mathbf{w}_1$ and $\mathbf{w}_2$. Each of them involves the vorticity tensor

$$\omega_{\alpha\gamma}=\partial_\gamma\left(\frac{u_\alpha}{\rho}\right)-\partial_\alpha\left(\frac{u_\gamma}{\rho}\right), \tag{7.36}$$

the dissipative Navier-Stokes-like terms arising due to gradients of the overall and relative momenta, and the nondissipative internal structure contribution

$$\left(\frac{\partial w_{1\alpha}}{\partial t}\right)^{(ie)}=c_1\int d\mathbf{R}\psi\partial_\alpha\Phi_\psi-c_1\partial_\beta\left(\int d\mathbf{R}\psi R_\beta\frac{\partial}{\partial R_\alpha}(\Phi_\psi)\right) \tag{7.37}$$

$$\left(\frac{\partial w_{2\alpha}}{\partial t}\right)^{(ie)}=c_2\int d\mathbf{R}\psi\partial_\alpha\Phi_\psi-c_2\partial_\beta\left(\int d\mathbf{R}\psi R_\beta\frac{\partial}{\partial R_\alpha}(\Phi_\psi)\right) \tag{7.38}$$

if ψ is used as the state variable and

$$\left(\frac{\partial w_{1\alpha}}{\partial t}\right)^{(ie)}=c_1m_{\beta\gamma}\partial_\alpha\Phi_{m_{\beta\gamma}}-c_1\partial_\beta\left(2m_{\beta\gamma}\Phi_{m_{\gamma\alpha}}\right) \tag{7.39}$$

$$\left(\frac{\partial w_{2\alpha}}{\partial t}\right)^{(ie)}=c_2m_{\beta\gamma}\partial_\alpha\Phi_{m_{\beta\gamma}}-c_2\partial_\beta\left(2m_{\beta\gamma}\Phi_{m_{\gamma\alpha}}\right) \tag{7.40}$$

if $\mathbf{m}$ is used. It is important to observe that these two equations involve explicitly the gradients of the chemical potentials of the three components composing the ternary mixture (i.e. the third and fourth terms on the right hand sides of the w_1 and w_2 equations). We will show in the next section, when studying the asymptotic solutions (the approach to equilibrium), that these terms turn out to be essential for giving rise to both the main and the cross coupling phenomena in the mass diffusion fluxes of the two components. We emphasize that these couplings arise from the Poisson side (the reversible part) of GENERIC and thus emerge naturally in the governing equations without any assumption. The last three terms in these two equations express the dissipation.

The remaining equations in (7.23) and (7.24) describe the time evolution of the internal structure. We have shown that, in the case of pure diffusion (i.e. if no external flow is applied) of a solvent in a polymer that can swell, the terms involving the relative velocity, i.e. Φ_w, try to extend (swell) the polymer network [41]. A similar situation is expected to arise also in the context of two solvents. The swelling will remain finite due to the presence of the relaxation recovery of the network expressed in the last term on the right hand side of the internal structure governing equation. This appears clearly in particular in the $\mathbf{m}$-equation. The last term in this equation, accounting for dissipation, is a highly nonlinear term in $\mathbf{m}$. The choice that we made for this term is supported by the fact that for small relaxation times τ of the internal structure ($\lambda = 1/(\tau G)$, G is the elastic modulus of the polymer network) we recover the Newtonian regime. λ is generally a tensorial quantity, especially in media where anisotropy effects become more significant. For simplicity, we chose it here to be a scalar function that may depend ,among others, on concentrations of the two components.

We recall that the governing equations (7.22)-(7.40) have been introduced above as a particular realization of GENERIC (7.1). They involve quantities, namely the free energy Φ and the kinetic coefficients introduced in the dissipation potential, that still

remain unspecified. We shall denote them by the symbol $\wp$ representing the parameter space of the family of the equations (7.22)-(7.40).

Having derived the governing equations, we can now look into their consequences that can be compared with experimental observations. This task will be the subject of the next section. We shall see that this type of analysis provides also an insight into the physical interpretation of the kinetic coefficients.

Another interesting problem that we may look at is the problem of relating the governing equations (7.22)-(7.40) to the governing equations of a more microscopic theory. For example, a theory in which the states of all molecules composing the fluids under consideration are used to describe its time change behavior. Here, we shall only recall an interesting paper of Bearman [42] in which the molecular-theory basis of diffusion is discussed. Bearman has introduced in his analysis the friction coefficients [42,43] ξ^*_{ij} by

$\partial_\alpha \mu_i = -\sum_j \frac{\rho_j N_A^2}{M_j M_i} \xi^*_{ij} (v_{i\alpha} - v_{j\alpha})$ where μ_i is the chemical potential per unit mass of the i-th component, N_A is the Avogadro's number ρ_j and M_j denote the mass density and molecular weight of the component j, respectively. v_i is the velocity of the component i. Straightforward calculations then lead to the following relation

$$\begin{aligned} \Lambda_1 &= \rho c_1 \left((1 - c_1 - c_2) \xi_{1p} + c_2 \xi_{12} \right) \\ \Lambda_2 &= \rho c_2 \left((1 - c_1 - c_2) \xi_{2p} + c_1 \xi_{12} \right) \\ \Lambda_{12} &= -\rho c_1 c_2 \xi_{12} \end{aligned} \qquad (7.41)$$

between the kinetic coefficients Λ_{ij} introduced in (7.21) and the coefficients ξ_{ij} related to the Bearman friction as $\xi_{ij} = \frac{\rho N_A^2}{M_i M_j} \xi^*_{ij}$. In view of the symmetry property of ξ^*_{ij}, ξ_{ij} and therefore also Λ_{ij} satisfy the symmetry property required in GENERIC.

7.4. ASYMPTOTIC SOLUTIONS

We begin now to discuss solutions to the family (7.22)-(7.40) of the time evolution equations and compare them with results of experiments. We start with properties that hold for all points in the parameter space $\wp$. Gradually, we shall proceed to properties that hold only for some regions in $\wp$ and, eventually, study numerical solutions that require a specific choice of a point in $\wp$.

7.4.1 Compatibility with Equilibrium Thermodynamics

The first experimental observation with which we compare solutions to (7.22)-(7.40) is the following: Let the system under consideration be left free of external influences. Under these conditions, the system is observed to reach (as $t\to\infty$) a state, called a thermodynamic equilibrium state, at which its behavior is found to be well described by equilibrium thermodynamics. This observation is in fact an observation of the final stage of the diffusion. We thus want: (i) to identify thermodynamic equilibrium states in solutions of (7.22)-(7.40), (ii) to prove that these states are approached as $t\to\infty$, and (iii) to identify the fundamental thermodynamic relation implied by (7.22)-(7.40).

To solve these three problems, it is enough to recall that (7.22)-(7.40) have been introduced as a particular realization of GENERIC. The GENERIC structure itself guarantees that: (i) thermodynamic equilibrium states, denoted x_{th}, are solutions to

$$\Phi_x = 0 \tag{7.42}$$

x is either (7.6) or (7.7), (ii) the thermodynamic equilibrium states x_{th} are approached as $t\to\infty$ (this is proven by showing that the free energy Φ plays the role of the Lyapunov function associated with this approach), and (iii) the fundamental thermodynamic equation of state implied by (7.22)-(7.40) is

$$\Phi(x_{th}, T) = -PV \tag{7.43}$$

where T is the thermodynamic temperature, V is the volume, and P is the equilibrium thermodynamic pressure. All the above three results are proven for all points in the parameter space $\wp$.

7.4.2 Generalized Fickian Diffusion

In the previous subsection, we have looked at the final outcome of the diffusion. Now we turn our attention to the diffusion itself. We begin by the following well known observation: If the polymer component is replaced by another simple fluid or if the third component is in the rubbery state then the observed diffusion process is well described by a model [37-38] that generalizes Fick's model [44]. Our objective in this section is to recognize the region in $\wp$ in which solutions to (7.22)-(7.40) are well approximated by solutions to the governing equations of the generalized Fick model.

If $\lambda >> 1$ or $\Gamma >> 1$ then, as it follows from the equations in (7.23) and (7.24), the internal structure equilibrates very rapidly. We can thus assume that we look at the diffusion process already at the stage when the internal structure is equilibrated and as such, it does not participate actively in the diffusion process. If, moreover, we look at the region in $\wp$ in which $\Lambda_i >> 1$ and $\Lambda_{\tilde{i}} >> 1$, i,j =1,2, then we can put $dw_1/dt \approx 0$, $dw_2/dt \approx 0$. If in addition we ignore the quadratic terms involving w_1 and w_2 in the fifth and the sixth equation (7.22) and the term involving the rate of strain $\kappa_{\alpha\beta} = \partial v_\beta / \partial r_\alpha$ we arrive at

$$\Lambda\Phi_{w_\alpha} = \mathbf{A}\begin{pmatrix} \partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) \\ \partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) \end{pmatrix} \tag{7.44}$$

where Λ and $\mathbf{A}$ are the matrices defined above (see (7.21) and (7.35)). Written explicitly, (7.44) becomes

$$\Lambda_1\Phi_{w_{1\alpha}} + \Lambda_{12}\Phi_{w_{2\alpha}} = \rho c_1(1-c_1)\partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) - \rho c_1 c_2\partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) \tag{7.45}$$

$$\Lambda_{12}\Phi_{w_{1\alpha}} + \Lambda_2\Phi_{w_{2\alpha}} = \rho c_2(1-c_2)\partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) - \rho c_1 c_2\partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) \tag{7.46}$$

By resolving these equations for Φ_{w_1} and Φ_{w_2}, we obtain

$$\Phi_{w_\alpha} = \Lambda^{-1}\mathbf{A}\begin{pmatrix} \partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) \\ \partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) \end{pmatrix} = \Lambda^{-1}\mathbf{A}\mathbf{P}\begin{pmatrix} \partial_\alpha c_1 \\ \partial_\alpha c_2 \end{pmatrix} \tag{7.47}$$

where

$$\mathbf{P} = \frac{1}{\rho}\begin{pmatrix} \varphi_{c_1c_1} & \varphi_{c_1c_2} \\ \varphi_{c_2c_1} & \varphi_{c_2c_2} \end{pmatrix} \tag{7.48}$$

For the sake of simplicity and because we are interested here more particularly in the diffusion process, we have neglected terms involving $\varphi_{c_i\rho}$, i=1,2. Since

$\det \Lambda = \Lambda_1 \Lambda_2 - (\Lambda_{12})^2 > 0$, the matrix Λ is invertible. Inserting (7.47) into the expression (7.34), we obtain the mass flux

$$\mathbf{J}_\alpha = \mathbf{A}\,\Phi_{w_\alpha} = \mathbf{A}\Lambda^{-1}\mathbf{A}\,\mathbf{P}\begin{pmatrix}\partial_\alpha c_1\\ \partial_\alpha c_2\end{pmatrix} \tag{7.49}$$

which, after an appropriate rearrangement, becomes

$$\mathbf{J}_\alpha = -\rho\boldsymbol{\Omega}\begin{pmatrix}\partial_\alpha\left(\dfrac{\varphi_{c_1}}{\rho}\right)\\ \partial_\alpha\left(\dfrac{\varphi_{c_2}}{\rho}\right)\end{pmatrix} = -\rho\mathbf{D}\begin{pmatrix}\partial_\alpha c_1\\ \partial_\alpha c_2\end{pmatrix} \tag{7.50}$$

where

$$\boldsymbol{\Omega} = -\frac{1}{\rho}\mathbf{A}\Lambda^{-1}\mathbf{A} = \begin{pmatrix}\Omega_{11} & \Omega_{12}\\ \Omega_{21} & \Omega_{22}\end{pmatrix} \tag{7.51}$$

and

$$\mathbf{D} = -\frac{1}{\rho}\mathbf{A}\Lambda^{-1}\mathbf{A}\mathbf{P} = \begin{pmatrix}D_{11} & D_{12}\\ D_{21} & D_{22}\end{pmatrix} \tag{7.52}$$

We see clearly that the matrix $\boldsymbol{\Omega}$ is symmetric (since both Λ and $\mathbf{A}$ are symmetric matrices) while the matrix $\mathbf{D}$ of the diffusion coefficients is not symmetric. If we write explicitly the mass density fluxes as functions of D_{ij}, expression (7.50) becomes

$$J_{1\alpha} = -\rho D_{11}\partial_\alpha c_1 - \rho D_{12}\partial_\alpha c_2 \tag{7.53}$$

$$J_{2\alpha} = -\rho D_{21}\partial_\alpha c_1 - \rho D_{22}\partial_\alpha c_2 \tag{7.54}$$

where the coefficients of the matrix $\mathbf{D}$ are given by

$$D_{11}=\frac{\rho}{\det\Lambda}\left[c_1^2\left((1-c_1)\Lambda_2+c_2\Lambda_{12}\right)\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,P,c_2}-c_1c_2\left(c_2\Lambda_1+(1-c_1)\Lambda_{12}\right)\left(\frac{\partial\mu_2}{\partial c_1}\right)_{T,P,c_2}\right]$$

$$D_{12}=\frac{\rho}{\det\Lambda}\left[c_1^2\left((1-c_1)\Lambda_2+c_2\Lambda_{12}\right)\left(\frac{\partial\mu_1}{\partial c_2}\right)_{T,P,c_2}-c_1c_2\left(c_2\Lambda_1+(1-c_1)\Lambda_{12}\right)\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,P,c_1}\right]$$

$$D_{21}=\frac{\rho}{\det\Lambda}\left[c_2^2\left((1-c_2)\Lambda_1+c_1\Lambda_{12}\right)\left(\frac{\partial\mu_2}{\partial c_1}\right)_{T,P,c_2}-c_1c_2\left(c_1\Lambda_2+(1-c_2)\Lambda_{12}\right)\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,P,c_2}\right]$$

$$D_{22}=\frac{\rho}{\det\Lambda}\left[c_2^2\left((1-c_2)\Lambda_1+c_1\Lambda_{12}\right)\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,P,c_2}-c_1c_2\left(c_1\Lambda_2+(1-c_2)\Lambda_{12}\right)\left(\frac{\partial\mu_1}{\partial c_2}\right)_{T,P,c_1}\right] \tag{7.55}$$

In (7.55) we have used [45]

$$\rho(\mu_1-\mu_1^0)=\varphi+(1-c_1)\varphi_{c_1}-c_2\varphi_{c_2}$$
$$\rho(\mu_2-\mu_2^0)=\varphi+(1-c_2)\varphi_{c_2}-c_1\varphi_{c_1} \tag{7.56}$$

μ_i is the chemical potential per molecular weight of the i-th component, and μ_i^0 is a reference value chosen at the pure state. φ_{c_i} is the partial derivative of the internal free energy density with respect to the mass fraction of i-th component. Note also that $\det\Lambda=\Lambda_1\Lambda_2-(\Lambda_{12})^2>0$ (see Section 7.3.4). D_{ii} are the main (principal) diffusion coefficients and D_{ij} are the cross diffusion coefficient. We recall that these coefficients have been calculated in the reference frame moving with the center of mass [36-38]. In other reference frames, these coefficients assume a different form. The transformations involved can be easily found for example in [37-38]. The formulas for the diffusion coefficients expressed in terms of the friction coefficients (i.e. if expressions (7.41) are used to express Λ_{ij} in terms of the friction coefficients) are presented in Appendix.

Notice that the diffusion matrix in this linear regime is independent of the flow. We also note that the diffusion coefficients (7.55) reduce to their counterpart **D** in a binary mixture,

$$\mathbf{D} = \lim_{c_2 \to 0} \mathbf{D}_{11} = \frac{1}{\xi_{1p}} \left(\frac{\partial \mu_1}{\partial \ln c_1} \right) \tag{7.57}$$

Summing up, the governing equations of the generalized Fick's model are:

$$\begin{cases} \text{the first four equations in (7.22),} \\ \text{the mass fluxes (7.53) and (7.54)} \end{cases} \tag{7.58}$$

Now, we would like to see whether the approximations used to pass from (I.22)-(7.40) to (7.58) do not destroy the intrinsic compatibility of the governing equations with thermodynamics. We shall therefore show that Eqs.(7.58) represent a particular realization of GENERIC (7.1). If we succeed then we indeed prove that the GENERIC structure has been preserved.

We recall that in order to find out a realization of (7.1), one has to: (i) identify the set of the state variables x, (ii) find their Poisson kinematics, (iii) specify the dissipation potential, and (iv) specify the free energy. We begin by choosing the state variables $x^{(Fick)} = (\rho(r), u(r), c_1(r), c_2(r))$. Their Poisson kinematics can be easily obtained from (7.10). We note that if we restrict the functions A and B in (7.10) to those that depend only on $x^{(Fick)}$ then (7.10) reduces to the Poisson bracket

$$\{A,B\}^{(Fick)} = \int dr[\rho \partial_\alpha (A_\rho) B_{u_\alpha} + u_\gamma \partial_\alpha (A_{u_\gamma}) B_{u_\alpha} - A_{c_1} B_{u_\alpha} \partial_\alpha c_1 - A_{c_2} B_{u_\alpha} \partial_\alpha c_2 - A \leftrightarrow B] \tag{7.59}$$

Next, we introduce the following dissipation potential:

$$\Psi^{(\mathrm{Fick})} = \Psi^{(\mathrm{cfinFick})} + \Psi^{(\mathrm{cFick})} \tag{7.60}$$

where

$$\Psi^{(\mathrm{cfinFick})} = \Psi^{(\mathrm{cfin})}\,|_{\Lambda=0,\ \text{only } \eta \text{ and } \eta_\beta \text{ in (I.19) and (I.20) are different from zero}} \tag{7.61}$$

and

$$\Psi^{(\mathrm{cFick})} = \int d\mathbf{r}\left\{\left[\partial_\alpha\left(\frac{A_{c_1}}{\rho}\right),\partial_\alpha\left(\frac{A_{c_2}}{\rho}\right)\right]\frac{1}{2}\rho^2\Omega\left[\partial_\alpha\left(\frac{A_{c_1}}{\rho}\right),\partial_\alpha\left(\frac{A_{c_2}}{\rho}\right)\right]\right\}^{\tau} \tag{7.62}$$

Except the free energy Φ that is still left undetermined, we have now specified all what is needed in GENERIC. We can thus write down the governing equations. It is easy to verify that by inserting (7.59)-(7.62) into (7.1) we indeed arrive at the governing equations (7.58).

We emphasize that the observation made in the previous paragraph proves that Eqs.(7.58) are a particular realization of GENERIC and are thus compatible with thermodynamics. Equations (7.58) do not need the Eqs.(7.22) to justify them. The derivation of Eqs.(7.58) from Eqs. (7.22), presented at the beginning of this subsection, provides however an additional information. We see now, in the context of the more microscopic theory presented in Section 7.3, what is the domain of applicability of the generalized Fick theory. We have also shown how the matrix of diffusion coefficients **D** is expressed (see (7.51)-(7.56)) in terms of the quantities introduced in the dissipation potential of the more microscopic theory (see (7.12)-(7.21)).

7.4.3. Weakly Non-local Fickian Diffusion

Solvents are seen to propagate in glassy polymers as shock waves [46-48]. Since shock waves always involve large gradients, we conclude that experimental observations of anomalous diffusion motivate a closer look into the role that the first and higher order gradients play in the diffusion process. The formalism of GENERIC offers a particularly appropriate setting for making this investigation.

Following the idea that has been first introduced by Cahn an Hilliard[49], we let the free energy Φ depend on gradients of the solvent concentration. Everything that we did in Section 7.3 remains unchanged except that the functional derivative $\delta/\delta x$ has to be now replaced by the variational derivative $\delta/\delta x - \partial_\gamma \frac{\delta}{\delta(\partial_\gamma x)}$. This then brings about changes in the governing equations. Here, we shall work out explicitly the changes only in the context of the GENERIC setting of the Fickian diffusion (7.59)-(7.62).

It is easy to see that the new term in the equation governing the time evolution of u is: $\sum_{i=1,2} [-\partial_\alpha(c_i)\partial_\gamma(\Phi_{\partial_\gamma(c_i)})]$ which, as it can be directly verified, equals $\sum_{i=1,2} [\partial_\gamma\partial_\alpha(c_i)\Phi_{\partial_\gamma(c_i)} - \partial_\gamma(\partial_\alpha(c_i)\Phi_{\partial_\gamma(c_i)})]$. The first term becomes a part of the gradient of the scalar hydrodynamic pressure, the second term implies that a new elastic part of the extra stress tensor

$$\sigma_{\alpha\beta} = \sum_{i=1,2} \partial_\alpha(c_i)\Phi_{\partial_\beta(c_i)} \tag{7.63}$$

arises. The mixture thus behaves, from the rheological point of view, as a viscoelastic fluid even if all the fluids composing the mixture are simple (i.e. without an internal structure). Also the expression (7.50) for the mass flux changes. The derivative φ_{c_i} becomes the variational derivative $\varphi_{c_i} - \partial_\gamma(\varphi_{\partial_\gamma(c_i)})$, $i = 1,2$. This then also brings into the governing equations the higher order gradients.

We shall now show that the dependence of the free energy on the gradients of concentrations, that we have so far introduced phenomenologically, arises as a consequence of describing the Fickian diffusion in the context of the more microscopic setting of Section 7.3 (that involves also the relative momenta).

The free energy, on any level of description, has to involve always the kinetic energy. In the setting of Section 7.3 we thus write $\Phi = \int d\mathbf{r}\left[\frac{\mathbf{u}_1^2}{2\rho_1}+\frac{\mathbf{u}_2^2}{2\rho_2}+\frac{\mathbf{u}_p^2}{2\rho_p}\right]+\int d\mathbf{r}\varphi(\rho_1,\rho_2,\rho_p,\mathbf{m})$ which, in view of (7.4), becomes

$$\Phi = \int d\mathbf{r}\left(\left[\frac{\mathbf{u}^2}{2\rho}\right]+\left[\frac{a\mathbf{w}_1^2}{2\rho}+\frac{b\mathbf{w}_2^2}{2\rho}+\frac{d\mathbf{w}_1\mathbf{w}_2}{\rho}\right]\right)+\int d\mathbf{r}\varphi(\rho,c_1,c_2,\mathbf{m}) \tag{7.64}$$

where the first term represents the kinetic energy. We have used in (7.64) the following notation

$$a=\frac{1-c_2}{c_1(1-c_1-c_2)},\ b=\frac{1-c_1}{c_2(1-c_1-c_2)}\ \text{and}\ d=\frac{1}{(1-c_1-c_2)} \tag{7.65}$$

The term involving $\mathbf{u}$ expresses the overall kinetic energy, the terms involving $\mathbf{w}_i$ express the relative kinetic energy that stems from the relative motions between the three fluids composing the ternary mixture. The last term designates the Helmholtz free energy that is independent of velocities; φ is its density. We now derive some consequences of the choice (7.64).

First, we note that if we insert (7.64) into (7.32) and (7.33) we obtain

$$\mathbf{J}_1=\mathbf{w}_1\ \text{and}\ \mathbf{J}_2=\mathbf{w}_2 \tag{7.66}$$

The mass flux of the i-th component coincides thus exactly with its relative momentum density. Second, if we insert (7.53), (7.54) and (7.67) into (7.64), we obtain the free energy

$$\Phi = \int d\mathbf{r}\left[\frac{\mathbf{u}^2}{2\rho}\right] + \int d\mathbf{r}\left[\frac{1}{2}\rho\ell_{11}|\nabla c_1|^2 + \rho\ell_{12}\nabla c_1.\nabla c_2 + \frac{1}{2}\rho\ell_{22}|\nabla c_2|^2\right] + \int d\mathbf{r}\varphi(\rho, c_1, c_2) \tag{7.67}$$

that includes terms depending on gradients of the concentrations. In (7.67) we have used the following notation:

$$\begin{aligned}
\ell_{11} &= aD_{11}^2 + 2dD_{11}D_{21} + bD_{21}^2, \\
\ell_{12} &= aD_{11}D_{21} + d\left(D_{11}D_{22} + D_{12}D_{21}\right) + bD_{22}D_{21} \\
\ell_{22} &= aD_{12}^2 + 2dD_{22}D_{12} + bD_{22}^2
\end{aligned} \tag{7.68}$$

We have omitted the dependence of φ on $\mathbf{m}$ since we consider now only the Fickian diffusion in which the independent variables are (ρ, c_1,c_2, $\mathbf{u}$), and the fact that the mixing part is larger than the elastic part in the free energy. If (7.67) is restricted to binary mixtures then the second term, we shall denote it by the symbol $\Phi^{(ww)}$, becomes

$$\Phi^{(ww)} = \int d\mathbf{r}\left[\frac{\rho c_1}{2(1-c_1)(\xi_{1p})^2}\left(\frac{\partial \mu_1}{\partial c_1}\right)^2 |\nabla c_1|^2\right] \tag{7.69}$$

Similar expressions for the free energy have also been used in [10,13,15,18,19].

Now we turn our attention to the quadratic elastic stress tensor σ^{ww} given in (7.28) and discuss how the Fickean regime modifies it. This stress tensor, as discussed previously, is the sole term arising in the momentum balance equation that brings the

direct influence of the diffusion process on the flow behavior. Inserting (7.47) into (7.28) we arrive at

$$\sigma^{ww}_{\alpha\beta} = \rho\left(bD_{21}^2 + dD_{11}D_{21}\right)\partial_\alpha c_1\partial_\beta c_1 + \rho\left(bD_{21}D_{22} + dD_{12}D_{21}\right)\left(\partial_\alpha c_1\partial_\beta c_2 + \partial_\alpha c_2\partial_\beta c_1\right) + \rho\left(bD_{22}^2 + dD_{22}D_{12}\right)\partial_\alpha c_2\partial_\beta c_2 \tag{7.70}$$

which is the extra stress tensor associated with the diffusion process and the concentration fluctuations. We see thus that even if all the three components are simple, the diffusion process renders their mixture to behave, from the rheological point of view, as a viscoelastic fluid. The viscoelastic extra stress tensor is quadratic in the gradients of concentrations. This does not follow from the derivation of the Fickian diffusion presented in (7.59)-(7.62). We have however seen that we can arrive at the extra stress tensor of the type of (7.70), even in the context of the derivation following (7.59)-(7.62), provided we let the free energy to depend on gradients of the concentrations.

7.4.4 Generalized Non-Fickian Diffusion

As in Section 7.4.2 we shall still assume that $\Lambda_i >> 1$; $\Lambda_{ij} >> 1$, (i,j=1,2) $\kappa_{\alpha\beta} << 1$, $\partial w_1/\partial t \approx 0$, $\partial w_2/\partial t \approx 0$ (i.e. that w_1 and w_2 evolve rapidly towards equilibrium) but we shall keep the influence of the internal structure. Under these assumptions, the fifth and the sixth equations in (7.22) imply

$$\Lambda_1\Phi_{w_{1\alpha}} + \Lambda_{12}\Phi_{w_{2\alpha}} = \rho c_1(1-c_1)\partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) - \rho c_1 c_2\partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) + c_1 m_{\rho\gamma}\partial_\alpha\Phi_{m_{\rho\gamma}} + c_1\partial_\beta\sigma^{i.s.}_{\alpha\beta} \tag{7.71}$$

$$\Lambda_{12}\Phi_{w_{1\alpha}} + \Lambda_2\Phi_{w_{2\alpha}} = \rho c_2(1-c_2)\partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) - \rho c_1 c_2\partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) + c_2 m_{\beta\gamma}\partial_\alpha\Phi_{m_{\beta\gamma}} + c_2\partial_\beta\sigma^{i.s.}_{\alpha\beta} \quad (7.72)$$

From these expressions we then obtain, after straightforward calculations,

$$J_{1\alpha} = -\rho D_{11}\partial_\alpha c_1 - \rho D_{12}\partial_\alpha c_2 - \rho K_{1\beta\gamma}\partial_\alpha m_{\beta\gamma} + \rho E_1\partial_\beta\sigma^{i.s.}_{\alpha\beta} \quad (7.73)$$

$$J_{2\alpha} = -\rho D_{21}\partial_\alpha c_1 - \rho D_{22}\partial_\alpha c_2 - \rho K_{2\beta\gamma}\partial_\alpha m_{\beta\gamma} + \rho E_2\partial_\beta\sigma^{i.s.}_{\alpha\beta} \quad (7.74)$$

In addition to the four coefficients that have already arisen in the Fickian mass flux, four other new coefficients arise in the viscoelastic mass fluxes. The first two are second order tensors

$$K_{1\beta\gamma} = \frac{\rho}{\det\Lambda}\left[c_1^2\left((1-c_1)\Lambda_2 + c_2\Lambda_{12}\right)\left(\frac{\partial\mu_1}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2} - c_1c_2\left(c_2\Lambda_1 + (1-c_1)\Lambda_{12}\right)\left(\frac{\partial\mu_2}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2}\right]$$

$$K_{2\beta\gamma} = \frac{\rho}{\det\Lambda}\left[c_2^2\left((1-c_2)\Lambda_1 + c_1\Lambda_{12}\right)\left(\frac{\partial\mu_2}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2} - c_1c_2\left(c_1\Lambda_2 + (1-c_2)\Lambda_{12}\right)\left(\frac{\partial\mu_1}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2}\right] \quad (7.75)$$

and the remaining two are scalar functions of the mass fractions of the solvents.

$$E_1 = \frac{\rho}{\det\Lambda}\left[c_1^2\left((1-c_1)\Lambda_2 + c_2\Lambda_{12}\right) - c_1c_2\left(c_2\Lambda_1 + (1-c_1)\Lambda_{12}\right)\right]$$

$$E_2 = \frac{\rho}{\det\Lambda}\left[c_2^2\left((1-c_2)\Lambda_1 + c_1\Lambda_{12}\right) - c_1c_2\left(c_1\Lambda_2 + (1-c_2)\Lambda_{12}\right)\right] \quad (7.76)$$

D_{ij} are defined above in Eq. (7.55) but the chemical potentials include now the internal structure contributions and are given by

$$\rho(\mu_1-\mu_1^0)=\varphi+(1-c_1)\varphi_{c_1}-c_2\varphi_{c_2}-m_{ij}\varphi_{m_{ij}}$$
$$\rho(\mu_2-\mu_2^0)=\varphi+(1-c_2)\varphi_{c_2}-c_1\varphi_{c_1}-m_{ij}\varphi_{m_{ij}} \qquad (7.77)$$

Notice that due to the fact that the internal Helmholtz free energy can be written as a sum of a mixing part and an elastic part, i.e., $\varphi=\varphi^{(mix)}(c_1,c_2)+\varphi^{(elas)}(c_1,c_2,\mathbf{m})$, the chemical potential for the i-th component can be recast into the form $\mu_i=\mu_i^{mix}(c_1,c_2)+\mu_i^{elas}(c_1,c_2,\mathbf{m})$. Consequently, the diffusion matrix is a sum of two contributions, i.e., $\mathbf{D}_{coop}=\mathbf{D}_{mix}+\mathbf{D}_{elas}$. Both $\mathbf{D}_{mix}$ and $\mathbf{D}_{elas}$ are given by the expressions appearing in Eqs. (7.55) except that here, μ_i is replaced by μ_i^{mix} in the expression for $\mathbf{D}_{mix}$ and by μ_i^{elas} in the expression for $\mathbf{D}_{elas}$. The matrix $\mathbf{D}_{coop}$ of diffusion coefficients depends explicitly on the state variable $\mathbf{m}$ describing the internal structure and is understood as the cooperative diffusion matrix. In binary mixtures, it reduces to the scalar cooperative diffusion coefficient $D_{coop}=\frac{c_1}{\xi_{lp}}\left[\left(\frac{\partial\mu_1^{(mix)}}{\partial c_1}\right)+\left(\frac{\partial\mu_1^{(elas)}}{\partial c_1}\right)\right]$.

Next, we turn our attention to the second term on the right hand side of (7.65), i.e. to the part of the kinetic energy associated with the relative motion. If we replace $\mathbf{w}_1$ and $\mathbf{w}_2$ by the expressions implied by (7.73)-(7.74) and in view of (7.67) we arrive at

$$\Phi=\Phi^{(67)}+\int d\mathbf{r}\left[A\left|\nabla.\boldsymbol{\sigma}^{(is)}\right|^2+B_{ijkl}\partial_\alpha m_{ij}\partial_\alpha m_{kl}+C_{ij}\partial_\alpha m_{ij}\partial_\gamma\sigma_{\alpha\gamma}^{(i.s.)}+R_\alpha\partial_\gamma\sigma_{\alpha\gamma}^{(is)}+F_{ij\alpha}\partial_\alpha m_{ij}\right] \qquad (7.82)$$

The first term on the right hand side, given in (7.67), expresses the contribution of the Fickian concentration fluctuations of the two solvents. The second term in (7.82) accounts for fluctuations of the internal structure and for non-local effects. It arises only in the viscoelastic regime and can be regarded as representing the viscoelastic non-

Fickian fluctuations of the complex mixture caused by the presence of the polymeric chains. The multiplication factors involved in the second part of (7.82) are given by

$$
\begin{aligned}
A &= \frac{1}{2}\left(aE_1^2 + bE_2^2 + 2dE_1E_2\right)\\
B_{ijkl} &= 2\rho^2\left(aK_{1ij}K_{1kl} + bK_{1ij}K_{2kl} + 2dK_{1ij}K_{2kl}\right)\\
C_{ij} &= -\rho\left(aE_1K_{1ij} + bE_2K_{2ij} + 2\left(E_1K_{2ij} + E_2K_{1ij}\right)\right)\\
F_{ij\alpha} &= -\rho\left(aK_{1ij}J^F_{1\alpha} + bK_{2ij}J^F_{2\alpha} + 2d\left(K_{2ij}J^F_{1\alpha} + K_{1ij}J^F_{2\alpha}\right)\right)\\
R_\alpha &= \left(aE_1J^F_{1\alpha} + bE_2J^F_{2\alpha} + 2d\left(E_2J^F_{1\alpha} + E_1J^F_{2\alpha}\right)\right)
\end{aligned}
\tag{7.83}
$$

We have used the symbol J_i^F to denote the Fickian mass flux density of the i-th component defined by (7.53) and (7.54). Notice that the second term on the right hand side of (7.82) disappears in the absence of the solvents. This is obvious from the expressions (7.83). We thus see that the internal structure of the polymer fluctuates only due to the motion of the solvents.

Summing up, we see that if we restrict the investigation to the region of $\wp$ in which $\Lambda_{ij} >> 1$, i,j =1,2, $\kappa_{\alpha\beta} << 1$(the gradient of overall velocity are small) we can write the governing equations as follows:

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t} = -\partial_\alpha(u_\alpha)\\
&\frac{\partial u_\gamma}{\partial t} = -\partial_\alpha\left(\frac{u_\alpha u_\gamma}{\rho}\right) - \partial_\gamma p - \partial_\alpha \sigma_{\alpha\gamma}\\
&\rho\frac{\partial c_1}{\partial t} = -u_\alpha\partial_\alpha c_1 + \partial_\alpha\left(\rho D_{11}\partial_\alpha c_1 + \rho D_{12}\partial_\alpha c_2 + \rho K_{1\beta\gamma}\partial_\alpha m_{\beta\gamma} - \rho E_1\partial_\beta \sigma^{(m)}_{\alpha\beta}\right)\\
&\rho\frac{\partial c_2}{\partial t} = -u_\alpha\partial_\alpha c_2 + \partial_\alpha(\rho D_{21}\partial_\alpha c_1 + \rho D_{22}\partial_\alpha c_2 + \rho K_{2\beta\gamma}\partial_\alpha m_{\beta\gamma} - \rho E_2\partial_\beta \sigma^{(m)}_{\alpha\beta})
\end{aligned}
\tag{7.84}
$$

Eq. (7.26) determining the hydrodynamic pressure p

Eq. (7.31) determining the extra stress tensor in terms of m

Eq. (7.24) determining the time evolution of $\mathbf{m}$ but in the linear regime.

Eqs.(7.82),(7.83) determining the free energy.

7.4.5 Coupling with the flow : $\kappa_{\alpha\beta} > 1$

As in Section III.4, we shall still assume here that $\Lambda_i >> 1$, $\Lambda_{ij} >> 1$, (i,j=1,2) $\partial w_1/\partial t \approx 0$, $\partial w_2/\partial t \approx 0$, but we shall keep, in addition to the influence of the internal structure, also the influence of the gradient of the overall velocity $\kappa_{\alpha\beta}$. Under these assumptions, the fifth and the sixth equations in (7.22) imply

$$\Lambda_1 \Phi_{w_{1\alpha}} + \Lambda_{12} \Phi_{w_{2\alpha}} = \rho c_1 (1 - c_1) \partial_\alpha \left(\frac{\varphi_{c_1}}{\rho} \right) - \rho c_1 c_2 \partial_\alpha \left(\frac{\varphi_{c_2}}{\rho} \right) + c_1 m_{\beta\gamma} \partial_\alpha \Phi_{m_{\beta\gamma}} + c_1 \partial_\beta \sigma^{i.s.}_{\alpha\beta} - w_{1\gamma} \kappa_{\alpha\gamma} \tag{7.85}$$

$$\Lambda_{12} \Phi_{w_{1\alpha}} + \Lambda_2 \Phi_{w_{2\alpha}} = \rho c_2 (1 - c_2) \partial_\alpha \left(\frac{\varphi_{c_2}}{\rho} \right) - \rho c_1 c_2 \partial_\alpha \left(\frac{\varphi_{c_1}}{\rho} \right) + c_2 m_{\beta\gamma} \partial_\alpha \Phi_{m_{\beta\gamma}} + c_2 \partial_\beta \sigma^{i.s.}_{\alpha\beta} - w_{2\gamma} \kappa_{\alpha\gamma} \tag{7.86}$$

Using the expression (7.64) for the energy, the relative momenta of the two solvent become expressible in terms of their conjugate variables as

$$\begin{pmatrix} w_{1\gamma} \\ w_{2\gamma} \end{pmatrix} = \mathbf{A} \begin{pmatrix} \Phi_{w_{1\gamma}} \\ \Phi_{w_{2\gamma}} \end{pmatrix} \tag{7.87}$$

Rearranging Eqs.(7.86) in terms of $\begin{pmatrix} \Phi_{w_1} & \Phi_{w_2} \end{pmatrix}^T$ and in view of (7.87), we obtain

$$\Lambda^*_{1\alpha\gamma} \Phi_{w_{1\gamma}} + \Lambda^*_{12\alpha\gamma} \Phi_{w_{2\gamma}} = \rho c_1 (1 - c_1) \partial_\alpha \left(\frac{\varphi_{c_1}}{\rho} \right) - \rho c_1 c_2 \partial_\alpha \left(\frac{\varphi_{c_2}}{\rho} \right) + c_1 m_{\beta\gamma} \partial_\alpha \Phi_{m_{\beta\gamma}} + c_1 \partial_\beta \sigma^{i.s.}_{\alpha\beta}$$

(7.88)

$$\Lambda^{*}_{21\alpha\gamma}\Phi_{w_{1\gamma}} + \Lambda^{*}_{2\alpha\gamma}\Phi_{w_{2\gamma}} = \rho c_2(1-c_2)\partial_\alpha\left(\frac{\varphi_{c_2}}{\rho}\right) - \rho c_1 c_2 \partial_\alpha\left(\frac{\varphi_{c_1}}{\rho}\right) + c_2 m_{\beta\gamma}\partial_\alpha\Phi_{m_{\beta\gamma}} + c_2\partial_\beta\sigma^{i.s.}_{\alpha\beta}$$

(7.89)

where the tensor coefficients arising on the left hand side of (7.88) and (7.89) have the following expressions

$$\begin{aligned}
\Lambda^{*}_{1\alpha\gamma} &= \Lambda_1\delta_{\alpha\gamma} + \rho c_1(1-c_1)\kappa_{\alpha\gamma} \\
\Lambda^{*}_{12\alpha\gamma} &= \Lambda_{12}\delta_{\alpha\gamma} - \rho c_1 c_2\kappa_{\alpha\gamma} \\
\Lambda^{*}_{21\alpha\gamma} &= \Lambda_{21}\delta_{\alpha\gamma} - \rho c_1 c_2\kappa_{\alpha\gamma} \\
\Lambda^{*}_{2\alpha\gamma} &= \Lambda_2\delta_{\alpha\gamma} + \rho c_2(1-c_2)\kappa_{\alpha\gamma}
\end{aligned} \qquad (7.90)$$

They are a sum of the isotropic part involving the coefficients of the matrix Λ defined above and the non-isotropic part depending explicitly on the rate of strain $\kappa_{\alpha\beta}$ and expressing thus the influence of the flow. It is clear form (7.90) that if $\kappa_{\alpha\beta} << 1$, the analysis developed in Section (7.4.3) is recovered. Solving the equations (7.88) and (7.89) for $\left(\Phi_{w_1} \quad \Phi_{w_2}\right)^T$, and in view of the expressions for the diffusion mass fluxes (7.32) and (7.33), we arrive at the following equations

$$J_{1\alpha} = -\rho D^{*}_{11\alpha\gamma}\partial_\gamma c_1 - \rho D^{*}_{12\alpha\gamma}\partial_\gamma c_2 - \rho K^{*}_{1\beta\gamma\alpha}\partial_\varepsilon m_{\beta\gamma} + \rho E^{*}_{1\varepsilon\beta}\partial_\varepsilon\sigma^{i.s.}_{\alpha\beta} \qquad (7.91)$$

$$J_{2\alpha} = -\rho D^{*}_{21\alpha\gamma}\partial_\gamma c_1 - \rho D^{*}_{22\alpha\gamma}\partial_\gamma c_2 - \rho K^{*}_{2\beta\gamma\alpha}\partial_\varepsilon m_{\beta\gamma} + \rho E^{*}_{2\varepsilon\beta}\partial_\varepsilon\sigma^{i.s.}_{\alpha\beta} \qquad (7.92)$$

The diffusion fluxes involve non-isotropic transport matrices $\mathbf{D}^{*}$, $\mathbf{K}^{*}$ and $\mathbf{E}^{*}$. Their expressions have the same form as in (7.55) (7.75) and (7.76) respectively but now the

(2x2) matrix Λ (with scalar coefficients) is replaced by the (6x6) matrix Λ^* with coefficients given by the expressions (7.90). The anisotropy brought about by the matrix Λ^*, via the gradient of velocity $\kappa_{\alpha\beta}$, introduces anisotropy into the diffusion matrix **D**, which becomes now a tensorial quantity. Even in the absence of the internal structure contribution to the fluxes (e.g. in simple fluids for instance), diffusion behaves anisotropically and other non-zero diffusion fluxes are created via the off-diagonal coefficients of $\mathbf{D}^*$. Moreover, the transport coefficients $\mathbf{K}_1$ and $\mathbf{K}_2$ (see (7.75)) and $\mathbf{E}_1$ and $\mathbf{E}_2$ (see (7.76)) are found to be also influenced, due to their dependence on Λ^*, by the flow and become consequently higher order tensors. Their modulus is seen form the expressions to be diminished by the applied flow. This means that the transport coefficients measured under no applied flow diffusion will have greater values than their counterparts measured under flow. Such a difference is expected to be significant in the particular case when the shear rate values are larger than the friction coefficients.

The discussion presented above becomes more transparent in the simple case of binary mixtures submitted to a flow (if the simple component 2 is absent). The ternary transport tensors reduce to the following binary transport tensors as

$$\mathbf{D}^*_{\alpha\beta} = \lim_{c_2\to 0} \mathbf{D}^*_{11\alpha\beta} = \frac{1}{\xi_{1p}\delta_{\alpha\beta} + \kappa_{\alpha\beta}} \left(\frac{\partial \mu_1}{\partial \ln c_1}\right) = \frac{\mathbf{D}}{\delta_{\alpha\beta} + \frac{1}{\xi_{1p}}\kappa_{\alpha\beta}} \tag{7.93}$$

$$\mathbf{K}^*_{\alpha\beta\varepsilon\gamma} = \lim_{c_2\to 0} \mathbf{K}^*_{1\alpha\beta\varepsilon\gamma} = \frac{c_1}{\left(\xi_{1p}\delta_{\varepsilon\gamma} + \kappa_{\varepsilon\gamma}\right)} \left(\frac{\partial \mu_1}{\partial m_{\alpha\beta}}\right)_{T,p} = \frac{\mathbf{K}_{1\alpha\beta}}{\delta_{\varepsilon\gamma} + \frac{1}{\xi_{1p}}\kappa_{\varepsilon\gamma}} \tag{7.94}$$

$$\mathbf{E}^*_{\alpha\beta} = \lim_{c_2\to 0} \mathbf{E}^*_{1\alpha\beta} = \frac{c_1}{\xi_{1p}\delta_{\alpha\beta} + \kappa_{\alpha\beta}} = \frac{\mathbf{E}_1}{\delta_{\alpha\beta} + \frac{1}{\xi_{1p}}\kappa_{\alpha\beta}} \tag{7.95}$$

Such expressions, to the best of our knowledge, have not been reported before. What is new in that binary mixtures, or more generally multi-component mixtures, subjected to flow is that the transport coefficients become dependent on the gradient of the applied velocity $\kappa_{\alpha\beta}$ and consequently the diffusion becomes anisotropic. In summary, the non-linear behavior of the ternary mixture in the non-Fickean regime is described by the following governing equations

$$\frac{\partial \rho}{\partial t} = -\partial_\alpha (u_\alpha)$$

$$\frac{\partial u_\gamma}{\partial t} = -\partial_\alpha \left(\frac{u_\alpha u_\gamma}{\rho} \right) - \partial_\gamma p - \partial_\alpha \sigma_{\alpha\gamma}$$

$$\rho \frac{\partial c_1}{\partial t} = -u_\alpha \partial_\alpha c_1 + \partial_\alpha \left(\rho D^*_{11\alpha\gamma} \partial_\gamma c_1 + \rho D^*_{12\alpha\gamma} \partial_\gamma c_2 + \rho K^*_{1\beta\gamma\varepsilon\alpha} \partial_\varepsilon m_{\beta\gamma} - \rho E^*_{1\varepsilon\beta} \partial_\varepsilon \sigma^{i.s.}_{\alpha\beta} \right)$$

$$\rho \frac{\partial c_2}{\partial t} = -u_\alpha \partial_\alpha c_2 + \partial_\alpha (\rho D^*_{21\alpha\gamma} \partial_\gamma c_1 + \rho D^*_{22\alpha\gamma} \partial_\gamma c_2 + \rho K^*_{2\beta\gamma\varepsilon\alpha} \partial_\varepsilon m_{\beta\gamma} - \rho E^*_{2\varepsilon\beta} \partial_\varepsilon \sigma^{i.s.}_{\alpha\beta})$$

Eq. (7.26) determining the hydrodynamic pressure p
Eq. (7.31) determining the extra stress tensor in terms of **m**
Eq. (7.24) determining the time evolution of **m.**
Eqs.(7.82),(7.83) determining the free energy.
Eqs. (7.91), (7.92) determining the mass fluxes. (7.96)

Next, we turn our attention to Eq.(7.24) , i.e., the equation governing the time evolution of **m**. First, we shall assume, as we did in Section 7.4.3, that $\lambda >> 1$ and show that we recover from (7.24) the Newton expression for the extra stress tensor. If $\lambda >> 1$ (i.e. if the elastic effects are negligible) then we put in (7.24) $\partial m_{\alpha\beta} / \partial t \approx 0$ and obtain

$$\begin{aligned}\lambda m_{\alpha\gamma}\sigma^{(is)}_{\gamma\beta} = &-m_{\alpha\beta}\partial_\gamma\left(\Phi_{u_\gamma}\right)+m_{\gamma\alpha}\partial_\gamma\Phi_{u_\beta}+m_{\gamma\beta}\partial_\gamma\Phi_{u_\alpha}\\ &+m_{\alpha\beta}\partial_\gamma\left(c_1\Phi_{w_{1\gamma}}\right)-m_{\gamma\alpha}\partial_\gamma\left(c_1\Phi_{w_{1\beta}}\right)-m_{\gamma\beta}\partial_\gamma\left(c_1\Phi_{w_{1\alpha}}\right)\\ &+m_{\alpha\beta}\partial_\gamma\left(c_2\Phi_{w_{2\gamma}}\right)-m_{\gamma\alpha}\partial_\gamma\left(c_2\Phi_{w_{2\beta}}\right)-m_{\gamma\beta}\partial_\gamma\left(c_2\Phi_{w_{2\alpha}}\right)\end{aligned} \tag{7.97}$$

which implies

$$\begin{aligned}\sigma^{(is)}_{\alpha\beta} = \frac{1}{\lambda}[&-\delta_{\alpha\beta}\partial_\gamma\left(\Phi_{u_\gamma}\right)+\partial_\alpha\Phi_{u_\beta}+\partial_\beta\Phi_{u_\alpha}\\ &+\delta_{\alpha\beta}\partial_\gamma\left(c_1\Phi_{w_{1\gamma}}\right)-\partial_\alpha\left(c_1\Phi_{w_{1\beta}}\right)-\partial_\beta\left(c_1\Phi_{w_{1\alpha}}\right)\\ &+\delta_{\alpha\beta}\partial_\gamma\left(c_2\Phi_{w_{2\gamma}}\right)-\partial_\alpha\left(c_2\Phi_{w_{2\beta}}\right)-\partial_\beta\left(c_2\Phi_{w_{2\alpha}}\right)]\end{aligned} \tag{7.98}$$

$\lambda = 1/(\tau G) = \dfrac{1}{\eta_p}$ is the polymer viscosity. Since, following our terminology, $\sigma^{(\text{theo log y})} = -\sigma^{(is)}$ we indeed recover, if we ignore the solvent contribution and quadratic terms, the classical expression for the Newton extra stress tensor. However, we see that the bulk viscosity and the shear viscosity of the polymer, both overall and relative, appear to be identical. This is because we have assumed that λ is a scalar. In order to arrive at different bulk and shear viscosities we have to take into account the anisotropy of the polymeric medium. Such an improvement can be accomplished by considering the parameter λ to be a tensor. In such a case (7.98) would indeed imply different shear and bulk viscosities.

Now, we shall not assume that $\lambda >> 1$ and consider Eq.(7.24) in its entirety. In order to make our discussion more explicit, we shall now specify the free energy. First, we turn our attention to φ introduced in (7.64). We recall that

$$\varphi = \varphi^{(mix)} + \varphi^{(is)} \tag{7.99}$$

The first term on the right hand side of (7.99) is the free energy of mixing between the three fluids. It is usually chosen to be the familiar Flory energy expression [50]. The second term is the internal structure contribution. In order to specify it, we have to introduce a

model of the polymer macromolecules. The simplest such model is to regard the macromolecules as Hookean dumbbells. This may seem very simplistic for discussing complex problems such as those related to the concentration fluctuation in sheared polymer solutions. Since in such a case the polymeric chains may become highly entangled and a constitutive equation for the extra stress tensor and thus an appropriate expression for the elastic free energy are required. An adequate choice certainly lies in employing the Doi-Edwards model derived from the reptation theory [51]. However, in this subsection, our aim is to show how the time evolution for the internal structure described by the deformation second order tensor $\mathbf{m}$, transforms in terms of the polymer extra stress tensor σ, and how it is strongly modified by the relative motions of the other components. Thereby, we limit the expression of the elastic free energy to the following form

$$\varphi^{(ie)} = \frac{1}{2} G_0 \left(\mathrm{tr}\tilde{\mathbf{m}} - \ln \det \tilde{\mathbf{m}} \right) \tag{7.100}$$

We have used the dimensionless quantity $\tilde{\mathbf{m}} = \dfrac{\mathbf{m}}{m_0}$, $m_0 = k_B\, T/H$, where H is a characteristic elastic constant, k_B is the Boltzmann constant, T is the thermodynamic temperature, and G_0 is the elastic modulus. If H and G_0 are constants independent of the concentrations then the free energy (7.100) is not suitable for discussing the swelling. We have shown in [41], in the context of one solvent, how to modify the free energy of the type (7.100) in order to arrive at a setting appropriate for discussing the swelling effects on the diffusion process. The method developed in [41] can be generalized to the mixture involving two solvents. In this paper, we shall not however make these modifications.

The choice of the free energy (7.100) allows us to rewrite (7.96) into a more explicit form. Using (7.31), Eq.(7.100) implies

$$\sigma_{\alpha\beta}^{(ie)} = G_0 \left(\tilde{m}_{\alpha\beta} - \delta_{\alpha\beta} \right) \tag{7.102}$$

To simplify the notation we shall omit hereafter the superscript (is) denoting the internal structure. Eq. (7.102) constitutes a one-to-one transformation between σ and $\tilde{\mathbf{m}}$, and $\tilde{\mathbf{m}}$ can be thus expressed in terms of σ as

$$\tilde{m}_{\alpha\beta} = \frac{\sigma_{\alpha\beta}}{G_0} + \delta_{\alpha\beta} \tag{7.103}$$

Equation (7.24) can be thus rewritten as

$$\begin{aligned}\frac{\partial \sigma_{\alpha\beta}}{\partial t} + \lambda \sigma_{\alpha\gamma}\sigma_{\gamma\beta} + \lambda G_0 \sigma_{\alpha\beta} = &-\partial_\gamma\left(\sigma_{\alpha\beta}\left(\frac{u_\gamma}{\rho} - \frac{w_{1\gamma}+w_{2\gamma}}{\rho(1-c_1-c_2)}\right)\right) + \sigma_{\gamma\alpha}\partial_\gamma\left(\frac{u_\beta}{\rho} - \frac{w_{1\beta}+w_{2\beta}}{\rho(1-c_1-c_2)}\right) \\ &+ \sigma_{\gamma\beta}\partial_\gamma\left(\frac{u_\alpha}{\rho} - \frac{w_{1\alpha}+w_{2\alpha}}{\rho(1-c_1-c_2)}\right) - \delta_{\alpha\beta}G_0\partial_\gamma\left(\frac{u_\gamma}{\rho} - \frac{w_{1\gamma}+w_{2\gamma}}{\rho(1-c_1-c_2)}\right) \\ &+ G_0\partial_\alpha\left(\frac{u_\beta}{\rho} - \frac{w_{1\beta}+w_{2\beta}}{\rho(1-c_1-c_2)}\right) + G_0\partial_\beta\left(\frac{u_\alpha}{\rho} - \frac{w_{1\alpha}+w_{2\alpha}}{\rho(1-c_1-c_2)}\right)\end{aligned} \tag{7.104}$$

We note in particular that in (7.104) it is not the complete applied velocity $\mathbf{v} = \frac{\mathbf{u}}{\rho}$ that influences the polymer. It is rather $\mathbf{v}_p = \frac{\mathbf{u}}{\rho} - \frac{\mathbf{w}_1 + \mathbf{w}_2}{\rho(1-c_1-c_2)}$ that acts directly on the polymer chains.

7.5. CONCLUDING REMARKS

In this paper, we have extended to ternary mixtures (of two simple and one complex fluids) the analysis of diffusion and rheology that we have developed previously in [18] for binary mixtures (of one simple and one complex fluids). The time evolution equations (7.22)-(7.40) derived in this paper extend directly the equations (4.61)-(4.75) derived in [18]. Our aim is to provide a setting suitable for studying complex phenomena

that arise only in multi-component mixtures (e.g. composition changes caused by cross-couplings among diffusion processes and the overall flow). The quantities chosen to describe states of the ternary mixture in our mathematical formulation are: the overall mass density and momentum, concentrations of two components, two relative momenta, and the configuration space distribution function or the conformation tensor describing the internal structure of the polymeric component.

The general strategy that we use for writing down the governing equation is the same as the one we have used in [18]. We begin with a general framework (GENERIC) that by itself guarantees agreement of solutions of the governing equations with results of certain basic experimental observations. In the second stage, the framework is filled out with the physical insight expressing the individual features of the system under consideration. Advantages of this two-stage modeling appear even more clearly in the context of more complex ternary mixtures than they appeared in the context of binary mixtures.

Having derived the governing equations, we proceed to solve them and compare the solutions with results of experimental observations.

First, we turn our attention to the observation according to which ternary mixtures, if left without the influence of external forces, reach a state, called an equilibrium state, at which their behavior is seen to be well described by equilibrium thermodynamics. We are then also interested to find out what is the fundamental thermodynamic relation implied by the governing equations. One of the advantages of the two-stage modeling that we have followed is that the agreement with this experimental observation is guaranteed. We also know the fundamental thermodynamic equation implied by the time evolution equations.

Next, we have looked at the particular situation in which the internal structure as well as the relative momenta evolve much faster than the rest of the state variables. If this is the case then the diffusion process is experimentally observed to follow the generalized Fickean description, which we show to be indeed implied by the governing equations (7.22)- (7.40). Since we consider systematically also the time evolution equation of the

overall momentum, we derive also the rheology implied by the diffusion. We show that the mixture is viscoelastic due to the diffusion even if all the components are simple inelastic fluids. The elastic part of the stress tensor appears to be quadratic in the gradients of concentrations. We have also shown how the higher order gradients arise in the Fickean diffusion and how they translate into the viscoelastic rheological behavior.

Second, we consider in this paper the situation that corresponds, now in the context of ternary mixtures and the presence of the overall flow, to the situation previously described by the classical non-Fickean models [9-20] in binary mixtures. Only the relative momenta evolve faster than the rest of the state variables. This means that the time evolution of the internal structure of the polymeric component stays in the model, only the relative momenta become dependent state variables. In this way, we arrive at the governing equations that directly extend (to include three components, an overall flow and thus rheology, and the internal structure in an explicit way) the governing equations of the classical non-Fickean models derived previously for binary systems.

In the first and the second points summarized above, the gradients $\kappa_{\alpha\beta}$ of the overall velocity are regarded to be too small to contribute to the asymptotic solutions of the time evolution of the diffusion mass fluxes. In that case, the calculated transport coefficients can be regarded as independent of the flow effects. Therefore, their values in systems undergoing flow can be safely approximated by their measured values in the absence of the flow (i.e., obtained by the chemical diffusion measurements). In the final point, we have discussed the non-linear regime in which the gradients $\kappa_{\alpha\beta}$ of the overall velocity are not too small to be ignored. We have showed that the transport coefficients (cooperative diffusion tensors, etc.) depend explicitly, in this non-linear regime, on $\kappa_{\alpha\beta}$. Even in simple fluids, the coefficients of the diffusion matrix $\mathbf{D}$ become second order tensor $\mathbf{D}^*$, and the flow induces anisotropy in the process of diffusion. The non-vanishing off-diagonal coefficients of $\mathbf{D}^*$ give rise to additional non zero-components of the diffusion mass fluxes.

In the following paper, we proceed to a more detailed analysis (including the numerical results) of solutions to the governing equations (7.22)-(7.40) in the absence of overall flow and to the comparison of the solutions with experimental observations of the diffusion processes.

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7.7. Appendix

The determinant of the matrix Λ given by (I.21) is expressed in terms of ξ_{ij} as

$$\det\Lambda = \rho^2 c_1 c_2 \left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right] \geq 0 \qquad \text{(A.7.1)}$$

where $c_p = 1 - c_1 - c_2$ is the polymer mass fraction. The diffusion coefficients can be written as functions of ξ_{ij}

$$D_{11} = \frac{1}{\left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right]}\left[c_1\left((1-c_1)\xi_{2p} + c_1\xi_{12}\right)\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,P,c_2} - c_1c_2\left(\xi_{1p} - \xi_{12}\right)\left(\frac{\partial \mu_2}{\partial c_1}\right)_{T,P,c_2}\right]$$

$$D_{12} = \frac{1}{\left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right]}\left[c_1\left((1-c_1)\xi_{2p} + c_1\xi_{12}\right)\left(\frac{\partial \mu_1}{\partial c_2}\right)_{T,P,c_2} - c_1c_2\left(\xi_{1p} - \xi_{12}\right)\left(\frac{\partial \mu_2}{\partial c_2}\right)_{T,P,c_1}\right]$$

$$D_{21} = \frac{1}{\left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right]}\left[c_2\left((1-c_2)\xi_{1p} + c_2\xi_{12}\right)\left(\frac{\partial \mu_2}{\partial c_1}\right)_{T,P,c_2} - c_1c_2\left(\xi_{2p} - \xi_{12}\right)\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,P,c_2}\right]$$

$$D_{22} = \frac{1}{\left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right]}\left[c_2\left((1-c_2)\xi_{1p} + c_2\xi_{12}\right)\left(\frac{\partial \mu_2}{\partial c_2}\right)_{T,P,c_2} - c_1c_2\left(\xi_{2p} - \xi_{12}\right)\left(\frac{\partial \mu_1}{\partial c_2}\right)_{T,P,c_1}\right]$$

(A.7.2)

The first two are second order tensors given by (7.75) are

$$K_{1\beta\gamma} = \frac{1}{\left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right]}\left[c_1\left((1-c_1)\xi_{2p} + c_1\xi_{12}\right)\left(\frac{\partial \mu_1}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2} - c_1c_2\left(\xi_{1p} - \xi_{12}\right)\left(\frac{\partial \mu_2}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2}\right]$$

$$K_{2\beta\gamma} = \frac{1}{\left[c_p \xi_{1p} \xi_{2p} + \xi_{12}\left(c_1\xi_{1p} + c_2\xi_{2p}\right)\right]}\left[c_2\left((1-c_2)\xi_{1p} + c_2\xi_{12}\right)\left(\frac{\partial \mu_2}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2} - c_1c_2\left(\xi_{2p} - \xi_{12}\right)\left(\frac{\partial \mu_1}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2}\right]$$

(A.7.3)

The parameters E_1 and E_2 expressed by Eq.(7.76) are

$$E_1 = \frac{c_1(1-c_1)\xi_{2p} - c_1c_2\xi_{1p} + c_1(c_1+c_2)\xi_{12}}{c_p\xi_{1p}\xi_{2p} + \xi_{12}(c_1\xi_{1p} + c_2\xi_{2p})}$$

$$E_2 = \frac{c_2(1-c_2)\xi_{1p} - c_1c_2\xi_{2p} + c_1(c_1+c_2)\xi_{12}}{c_p\xi_{1p}\xi_{2p} + \xi_{12}(c_1\xi_{1p} + c_2\xi_{2p})} \qquad \text{(A.7.4)}$$

In case of a binary mixture consisting of a solvent and a polymer, we find out that

$$\lim_{c_2\to 0} K_{1\alpha\beta} = \frac{c_1}{\xi_{1p}}\left(\frac{\partial\mu_1}{\partial m_{\alpha\beta}}\right)_{T,p}$$

$$\lim_{c_2\to 0} E_2 = 0$$

$$\lim_{c_2\to 0} E_1 = \frac{c_1}{\xi_{1p}} \qquad \text{(A.7.5)}$$

CHAPITRE 8

MIXTURE OF TWO SIMPLE AND ONE COMPLEX FLUIDS: II. DIFFUSION

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8.1 Abstract

We have derived a new model suitable for describing both standard and non-standard isothermal diffusion into two-solvent/polymer ternary mixtures under no overall flow and in mechanical equilibrium. The state variables are chosen to be: the scalar mass fractions c_1 and c_2 of the two simple fluids, their vectors mass fluxes $\mathbf{w}_1$ and $\mathbf{w}_2$ and a second order symmetric tensor $\mathbf{m}$ characterizing the deformation of the internal structure. The individual features of the mixture under consideration are expressed in the free energy and in the matrix of relaxation times. Solutions of the governing equations are discussed in detail by using both analytical considerations and numerical analysis. Propagation of linear waves of the solvents is investigated analytically and explicit formulas for the phase velocities and the attenuation intensity are provided. In the high frequency limit, the waves are found to propagate with constant, frequency independent, velocities. Detailed numerical solutions are found and compared with results of two types of experimental observations: (i) measurements of the pervaporation process of toluene-benzene mixture by a poly(ethylene terephthalate) rubbery membrane, and (ii) measurements of sorption profiles in a mixture of two solvents, one exhibiting the Fickian diffusion and the other the Case II diffusion, penetrating a glassy polymer.

8.2. Introduction

In this paper, we consider the time evolution of a mixture of two simple and one complex fluids under the condition of no overall flow, overall incompressibility, constant temperature, and mechanical equilibrium. This type of mixtures arises in many engineering applications (pervaporation, drug delivery systems, drying, coating, etc.). Experiments show that:

(i) In binary simple fluids, the time evolution is found to be well described by the Fickian diffusion.

(ii) In binary mixtures of one solvent and one polymer, the diffusion can be either Fickian or non-Fickian. The extreme case of the non-Fickian diffusion is the so-called Case II mass transport [1,2] in which the solvent enters the polymer as a shock wave. This type of diffusion is observed in glassy polymers in which the rearrangements needed to accommodate the solvent are relatively slow. Another consequence of such rearrangements is creation of internal stresses in the polymer that often cause cracks [1-3].

(iii) In ternary mixtures, many new phenomena are observed. For example, solvents that do not permeate through some polymer membranes are observed to contribute to the overall permeation mass flux when mixed with others [3-11]. In many applications, the difference in the permeation velocities and an adequate choice of the mixture composition in the feed are used to achieve separation [3-11]. The sorption process of a binary solvents into a glassy polymer has been seen in some mixtures to change continuously from the Case II to the Fickian type (or vice versa) by changing the composition of the mixture in the polymer [12]. Another interesting observation is reported for some polymer gels in which a volume phase transition occurs, upon changing the composition of the binary solvents in which they are immersed [13-14].

Our aim is to formulate a model suitable for describing the observed phenomena in ternary complex mixtures. In this paper, we shall remain on the mesoscopic level of description, namely the level on which the classical Fickian model of diffusion is formulated. How should the Fickian model be extended in order to include also the non-

Fickian behavior? It has been demonstrated [15-20] that the simple modification that enlarges considerably the domain of applicability of the original Fickian model is based on the assumption that the diffusion flux is proportional to the gradient of the chemical potential of the solvent rather than to its gradient of concentration. Since the internal free energy and thus the chemical potential depends also on the internal structure of the polymeric medium, the diffusion process becomes coupled to the internal deformations taking place in the polymeric medium. It is well known that the physical origin of such an improvement is based on the requirement of the mathematical compatibility of the diffusion process with equilibrium thermodynamics (i.e. the observation that, in the absence of external forces, the diffusion process brings eventually the mixture into a state at which its behavior is found to be well described by equilibrium thermodynamics). The success of the thermodynamic considerations in modeling diffusion processes suggests to try and take the thermodynamic considerations more seriously and more systematically. It is GENERIC [21-22] that attempts to express the compatibility with thermodynamics in a very systematic and thorough manner. We shall therefore apply the GENERIC formalism to diffusion in ternary complex mixtures. We have already done it in [20] in the context of binary mixtures of one solvent and one polymer . we have been indeed able to extend the domain of applicability of the classical non-Fickean models. In [Part I, chapter 7] of this series of two papers, we have formulated the governing equations for ternary mixtures undergoing an external flow. In this paper, we continue to analyze their predictions in the absence of the overall flow.

The state variables that we use to describe states of the mixture are the mass fractions of the two simple fluids, their diffusion mass fluxes and a quantity characterizing the internal structure of the complex fluid component. The model is expected to be physically realistic and at the same time simple enough so that complete solutions of its governing equations can be relatively easily obtained and compared with results of experimental observations. We begin our analysis with the governing equations (7.22)-(7.40) derived in Part I, chapter 7. Under the conditions of no overall flow, overall incompressibility, and mechanical equilibrium, theses equations (i.e. (7.22)-(7.40))

reduce to the governing equations (See Section 8.3) constituting the basis of this paper. We then proceed to solve them systematically.

First, we simplify them by considering a particular situation in which the diffusion fluxes evolve much faster than the rest of the state variables. The diffusion fluxes equilibrate rapidly and consequently become dependent state variables. The model that we obtain in this way is an extension, of the classical non-Fickean models derived previously for solvent-polymer binary mixtures [15-20], to two-solvents-polymer ternary mixtures.

Next, we consider the situation in which, in addition to diffusion fluxes, also the internal structure of the complex fluid component evolves rapidly and becomes a dependent state variable. The resulting model is a generalized Fickian model involving the cross coupling of the diffusion fluxes. Predictions based on this model are calculated numerically and compared with experimental observations, taken from the literature, of a specific pervaporation process.

Finally, we consider another particular situation in which the concentrations and diffusion fluxes remain independent state variables, only the internal structure of the complex fluid component is a dependent state variable. In the context of the mixture of one simple and one complex fluids, this formulation has been found [20] to be particularly suitable for describing both Fickian and non Fickian diffusion processes. In this paper, we thus extend this type of model to three components. We also analyze analytically the linear wave propagation (propagation of small disturbances in concentrations and diffusion fluxes). Explicit Formula for the dispersion relation and the phase velocity are calculated. A numerical solution of these governing equations is provided for a one dimensional sorption experiment of a binary mixture of a Case II solvent and a Fickean solvent into a glassy polymer.

8.3. Governing equations

The ternary mixture under consideration consists of two simple fluids (e.g. gases, solvents, etc.) and one complex fluid (e.g. polymer). Using the three-fluid model (see Part I, chapter 7), each component is described by its own mass density ρ_i and its own linear momentum density $\mathbf{u}_i$, (i = 1,2,p; 1,2 stand for the simple fluid components 1 and 2, p stands for "polymer", i.e. for the complex fluid component). States of the complex fluid component are, in addition, characterized by a symmetric second order tensor, called a *conformation tensor*, denoted by the symbol $\mathbf{m}$. The set of the state variables of the ternary mixture is therefore $(\rho_1, \mathbf{u}_1, \rho_2, \mathbf{u}_2, \rho_p, \mathbf{u}_p, \mathbf{m})$. As in Part I (chapter 7), we transform these variables into a new set

$$(\rho, \mathbf{u}, c_1, \mathbf{w}_1, c_2, \mathbf{w}_2, \mathbf{m}) \tag{8.1}$$

by the following one-to-one transformation

$$\rho = \rho_1 + \rho_2 + \rho_p$$

$$\mathbf{u} = \mathbf{u}_1 + \mathbf{u}_2 + \mathbf{u}_p$$

$$c_1 = \frac{\rho_1}{\rho_1 + \rho_2 + \rho_p}, \quad c_2 = \frac{\rho_2}{\rho_1 + \rho_2 + \rho_p} \tag{8.2}$$

$$\mathbf{w}_1 = \left(1 - \frac{\rho_1}{\rho}\right)\mathbf{u}_1 - \frac{\rho_1}{\rho}\mathbf{u}_2 - \frac{\rho_1}{\rho}\mathbf{u}_p$$

$$\mathbf{w}_2 = \left(1 - \frac{\rho_2}{\rho}\right)\mathbf{u}_2 - \frac{\rho_2}{\rho}\mathbf{u}_1 - \frac{\rho_2}{\rho}\mathbf{u}_p$$

where ρ is the overall mass density, $\mathbf{u}$ is the overall momentum density, c_i is the mass fraction of the component i and $\mathbf{w}_i$ denotes its relative momentum density.

The Helmholtz free energy is assumed to be

$$\Phi = \int d\mathbf{r}\left[\frac{\mathbf{u}_1^2}{2\rho_1} + \frac{\mathbf{u}_2^2}{2\rho_2} + \frac{\mathbf{u}_p^2}{2\rho_p}\right] + \int d\mathbf{r}\varphi(\rho_1, \rho_2, \rho_p, \mathbf{m}) \tag{8.3}$$

where the first term on the right hand side represents the kinetic energy and the density φ appearing in the second term, containing the mixing free energy and the contribution stemming from the complex fluid internal structure, is left at this point unspecified.

In the following, we aim at studying the processes of mass transport generated in the ternary mixture in the absence of applied flows; we restrict ourselves to the particular situation in which the overall momentum density equals zero

$$\mathbf{u} = 0 \tag{8.4}$$

and also to the mechanical equilibrium of the whole system, i.e.

$$\partial_\alpha p + \partial_\gamma \sigma_{\alpha\gamma}^{(\text{overall})} \equiv 0 \tag{8.5}$$

where p and σ represent the scalar pressure and extra stress tensor respectively (see [Part I, chapter 7]). We shall assume moreover the overall incompressibility, i.e.

$$\rho = \text{const.} \tag{8.6}$$

If the constraints (8.4)-(8.6) are introduced into (7.22), (7.24) appearing in [Part I, chapter 7] then we obtain the following time evolution equations

$$\rho \frac{\partial c_1}{\partial t} = -\partial_\alpha w_{1\alpha}$$

$$\rho \frac{\partial c_2}{\partial t} = -\partial_\alpha w_{2\alpha}$$

$$\frac{\partial w_{1\gamma}}{\partial t} = -\partial_\beta \left(w_{1\gamma} \frac{w_{1\beta}}{\rho c_1} \right) - c_1 \partial_\gamma \varphi_{c_1} - \Theta_{11} w_{1\gamma} - \Theta_{12} w_{2\gamma}$$

$$\frac{\partial w_{2\gamma}}{\partial t} = -\partial_\beta \left(w_{2\gamma} \frac{w_{2\beta}}{\rho c_2} \right) - c_2 \partial_\gamma \varphi_{c_2} - \Theta_{21} w_{1\gamma} - \Theta_{22} w_{2\gamma}$$

$$\frac{\partial m_{\alpha\beta}}{\partial t} = \partial_\gamma\left(m_{\alpha\beta}\frac{w_{1\gamma}}{\rho c_p}\right) - m_{\gamma\alpha}\partial_\gamma\left(\frac{w_{1\beta}}{\rho c_p}\right) - m_{\gamma\beta}\partial_\gamma\left(\frac{w_{1\alpha}}{\rho c_p}\right)$$
$$+\partial_\gamma\left(m_{\alpha\beta}\frac{w_{2\gamma}}{\rho c_p}\right) - m_{\gamma\alpha}\partial_\gamma\left(\frac{w_{2\beta}}{\rho c_p}\right) - m_{\gamma\beta}\partial_\gamma\left(\frac{w_{2\alpha}}{\rho c_p}\right) - 2\lambda m_{\alpha\gamma}m_{\gamma\varepsilon}\varphi_{m_{\varepsilon\beta}} \tag{8.7}$$

In the rest of this paper, we shall investigate consequences of these equations and compare them with results of experimental observations. We begin by discussing their physical content.

The first two equations are the mass continuity equations for the two solvents for which w_1 and w_2 represent their mass fluxes. Since, in view of the expression for the kinetic part of the free energy (i.e. the first part of Eq. (8.3)), the mass flux vector of each component coincides exactly with its relative momentum density vector

$$\rho c_1(1-c_1)\Phi_{w_1} - \rho c_1 c_2 \Phi_{w_2} = w_1$$
$$\rho c_2(1-c_2)\Phi_{w_2} - \rho c_1 c_2 \Phi_{w_1} = w_2 \tag{8.8}$$

which, in the matrix form, become

$$\mathbf{A}\begin{pmatrix}\Phi_{w_1}\\ \Phi_{w_2}\end{pmatrix} = \begin{pmatrix}w_1\\ w_2\end{pmatrix} \tag{8.9}$$

where the matrix A, defined also in [Part I, chapter 7], is given by

$$\mathbf{A} = \begin{pmatrix}\rho c_1(1-c_1) & -\rho c_1 c_2\\ -\rho c_1 c_2 & \rho c_2(1-c_2)\end{pmatrix} \tag{8.10}$$

The two following equations in (8.7) are the governing equations for the mass fluxes of the two fluids. Their irreversible part involves the phenomenological matrix

$$\Theta = \mathbf{A}^{-1}\Lambda = \begin{pmatrix} \Theta_{11} & \Theta_{12} \\ \Theta_{21} & \Theta_{22} \end{pmatrix} \tag{8.11}$$

where

$$\mathbf{A} = \begin{pmatrix} \Lambda_1 & \Lambda_{12} \\ \Lambda_{12} & \Lambda_2 \end{pmatrix} \tag{8.12}$$

is the matrix, positive definite and symmetric, of the relaxation phenomenological parameters (see [PartI, chapter 7]. Since $\det \mathbf{A} = \rho^2 c_1 c_2 c_p > 0$, $\mathbf{A}$ is invertible. The coefficients of the matrix Θ are :

$$\Theta_{11} = \frac{(1-c_2)\Lambda_1 + c_1\Lambda_{12}}{\rho c_1 c_p} \qquad \Theta_{12} = \frac{(1-c_1)\Lambda_{12} + c_2\Lambda_1}{\rho c_2 c_p}$$

$$\Theta_{21} = \frac{(1-c_2)\Lambda_{12} + c_1\Lambda_2}{\rho c_1 c_p} \qquad \Theta_{22} = \frac{(1-c_1)\Lambda_2 + c_2\Lambda_{12}}{\rho c_2 c_p} \tag{8.13}$$

Notice that contrary to the matrix Λ, the matrix Θ of the inverse of the relaxation times of the mass fluxes is not symmetric. The coefficients Θ_{11} and Θ_{22} are the inverse of the direct relaxation times, and Θ_{12} and Θ_{21} are the inverse of the coupling relaxation times. The relaxation coefficients (8.13) can also be expressed in terms of the friction coefficients $\xi_{ij}^{\bullet}$ arising in the Bearman theory [23-24]

$$\begin{aligned} \Theta_{11} &= (1-c_2)\xi_{1p} + c_2\xi_{12} \\ \Theta_{12} &= c_1(\xi_{1p} - \xi_{12}) \\ \Theta_{22} &= (1-c_1)\xi_{2p} + c_1\xi_{12} \\ \Theta_{21} &= c_2(\xi_{2p} - \xi_{12}) \end{aligned} \tag{8.14}$$

the coefficients ξ_{ij} appearing in the (8.14) are then related to Bearman's friction coefficients ξ_{ij}^* by $\xi_{ij} = \frac{\rho N_A^2}{M_i M_j}\xi_{ij}^*$, N_A is Avogadro's number, M_i is the molecular weight of the component i and ρ is the global mass density.

The last equation in (8.7) is the governing equation describing the time evolution for the internal structure. Its right hand side is a sum of two contributions, a reversible and an irreversible part. In the reversible part, the conformation tensor is advected by the vector $(-\mathbf{w}_1 - \mathbf{w}_2)/\rho c_p$ which stands, in fact, for the polymer velocity. The polymer internal structure moves then in the opposite direction to the solvent leading to the swelling of the polymer network. In the irreversible part the parameter λ is the phenomenological relaxation parameter (see more in [Part I, chapter 7]).

The family of the time evolution equations (8.7) is then completed by the internal structure contribution to the extra stress tensor

$$\sigma_{\alpha\beta}^{(i.s.)} = 2m_{\alpha\gamma}\Phi_{m_{\gamma\beta}} \tag{8.15}$$

which depends on the state variables (c_1, c_2, $\mathbf{m}$). In the following, for the sake of simplicity, the superscript (i.s.) will be omitted.

We shall call the model given by Eq. (8.7) a (c_1,c_2, $\mathbf{w}_1$,$\mathbf{w}_2$,$\mathbf{m}$)-model since (c_1, c_2, $\mathbf{w}_1$, $\mathbf{w}_2$, $\mathbf{m}$) play in it the role of independent state variables. The family of the time evolution equations (8.7) is parameterized by three parameters (φ, λ, Θ) which we regard as three coordinates of a parameter space to be denoted by the symbol $\wp$. Note that the coordinates of $\wp$ are functions, φ denotes the part of the Helmholtz free energy density that is independent of $\mathbf{w}_1$ and $\mathbf{w}_2$ (see (8.3)), Θ and λ are the phenomenological quantities related to the inverse of the relaxation times of ($\mathbf{w}_1$, $\mathbf{w}_2$) and $\mathbf{m}$ respectively.

The investigation of solutions to (8.7) is organized as follows. First, we identify regions in the parameter space $\wp$ in which solutions to (8.7) can be well approximated by

solutions to simpler (reduced) sets of equations. We begin by rearranging the third and fourth equations in (8.7)) into a new form

$$\frac{\partial w_{1\gamma}}{\partial t} = -\partial_\beta\left(\frac{w_{1\gamma}w_{1\beta}}{\rho c_1}\right) - c_1\varphi_{c_1c_1}\left[\partial_\gamma c_1 + R_1\partial_\gamma c_2 + L_{1\alpha\beta}\partial_\gamma m_{\alpha\beta}\right] - \Theta_{11}w_{1\gamma} - \Theta_{12}w_{2\gamma}$$

$$\frac{\partial w_{2\gamma}}{\partial t} = -\partial_\beta\left(\frac{w_{2\gamma}w_{2\beta}}{\rho c_2}\right) - c_2\varphi_{c_2c_2}\left[\partial_\gamma c_2 + R_2\partial_\gamma c_1 + L_{2\alpha\beta}\partial_\gamma m_{\alpha\beta}\right] - \Theta_{21}w_{1\gamma} - \Theta_{22}w_{2\gamma} \qquad (8.16)$$

where we have introduced two scalar coefficients

$$R_1(c_1,c_2,\mathbf{m}) = \frac{\varphi_{c_1c_2}}{\varphi_{c_1c_1}} \qquad (8.17)$$

$$R_2(c_1,c_2,\mathbf{m}) = \frac{\varphi_{c_1c_2}}{\varphi_{c_2c_2}} \qquad (8.18)$$

and two second order tensor coefficients

$$L_{1\alpha\beta}(c_1,c_2,\mathbf{m}) = \frac{\varphi_{c_1m_{\alpha\beta}}}{\varphi_{c_1c_1}} \qquad (8.19)$$

$$L_{2\alpha\beta}(c_1,c_2,\mathbf{m}) = \frac{\varphi_{c_2m_{\alpha\beta}}}{\varphi_{c_2c_2}} \qquad (8.20)$$

R_1, R_2, L_1 and L_2 depend on concentrations c_1 and c_2 of the solvents and also on the polymer structure characterized by $\mathbf{m}$. R_1 and R_2 couple the diffusion processes of the two simple fluids, whereas L_1 and L_2 couple diffusion of each component to the internal structure . φ introduced in (8.3) will be specified in Section (8.6). By $\varphi_{c_ic_j}$ we denote the second derivative of φ with respect to c_i and c_j (i,j=1,2) and $\varphi_{c_i\mathbf{m}}$ stands for the second derivative of φ with respect to c_i and $\mathbf{m}$.

8.4. Diffusion with m-inertia :(c_1,c_2,m)-model

8.4.1. General Formulation

Equations (8.7) can be interpreted as describing diffusion with triple inertia. The right hand side of the first two equations, i.e. "velocities" of c_1 and c_2, depend on both w_1 and w_2 that in turn depend on **m** through the second order tenors L_1 and L_2 (See (8.19) and (8.20)). Therefore, the continuity equation for each solvent i (i=1,2) is coupled directly to its mass flux governing equation and indirectly, through the parameters R_i, L_i and Θ, to the governing equations for the mass flux of the other component and to the internal structure, respectively. In this section, we look at the process of diffusion in the sub-regions of the parameter space where $\Theta_{ij} >> 1$ (i,j =1,2). In this region, the mass fluxes of the two simple fluid components relax faster than the internal structure. We recall that at equilibrium $\Phi_{w_1} = 0$ and $\Phi_{w_2} = 0$ which implies, in view of (8.3), that $w_1 = 0$ and $w_2 = 0$. If $\Theta_{ij} >> 1$, we can assume that $\frac{dw_i}{dt} \approx 0$ i =1,2 and diffusion becomes a process dominated by a single inertia stemming form **m**. Under these assumptions, Eqs.(8.16) reduce to

$$\Theta \begin{pmatrix} w_{1\alpha} \\ w_{2\alpha} \end{pmatrix} = G \begin{pmatrix} \partial_\alpha c_1 \\ \partial_\alpha c_2 \\ \partial_\alpha m_{\beta\gamma} \end{pmatrix} \tag{8.21}$$

where **G** is the matrix given by

$$G = \begin{pmatrix} c_1\varphi_{c_1c_1} & c_1\varphi_{c_1c_2} & c_1\varphi_{c_1m_{\beta\gamma}} \\ c_2\varphi_{c_2c_1} & c_2\varphi_{c_2c_2} & c_2\varphi_{c_2m_{\beta\gamma}} \end{pmatrix} \tag{8.22}$$

Θ is the relaxation time inverse matrix defined by (8.11) and (8.13). solving Equations (8.21) for w_1 and w_2 leads to

$$\begin{pmatrix} w_{1\alpha} \\ w_{2\alpha} \end{pmatrix} = \mathbf{D} \begin{pmatrix} \partial_\alpha c_1 \\ \partial_\alpha c_2 \\ \partial_\alpha m_{\beta\gamma} \end{pmatrix} \tag{8.23}$$

where **D** is the matrix of diffusion coefficients given by

$$\mathbf{D} = \begin{pmatrix} D_{11} & D_{12} & K_{1\alpha\beta} \\ D_{21} & D_{22} & K_{2\alpha\beta} \end{pmatrix} \tag{8.24}$$

where

$$\begin{aligned}
D_{11} &= \frac{1}{\det \Theta}\left[c_1\Theta_{22}\left(\frac{\partial \mu_{1p}}{\partial c_1}\right)_{T,P,c_2,m} - c_2\Theta_{12}\left(\frac{\partial \mu_{2p}}{\partial c_1}\right)_{T,P,c_2,m}\right] \\
D_{12} &= \frac{1}{\det \Theta}\left[c_1\Theta_{22}\left(\frac{\partial \mu_{1p}}{\partial c_2}\right)_{T,P,c_1,m} - c_2\Theta_{12}\left(\frac{\partial \mu_{2p}}{\partial c_2}\right)_{T,P,c_1,m}\right] \\
D_{21} &= \frac{1}{\det \Theta}\left[c_2\Theta_{11}\left(\frac{\partial \mu_{2p}}{\partial c_1}\right)_{T,P,c_2,m} - c_1\Theta_{21}\left(\frac{\partial \mu_{1p}}{\partial c_1}\right)_{T,P,c_2,m}\right] \\
D_{22} &= \frac{1}{\det \Theta}\left[c_2\Theta_{11}\left(\frac{\partial \mu_{2p}}{\partial c_2}\right)_{T,P,c_1,m} - c_1\Theta_{21}\left(\frac{\partial \mu_{1p}}{\partial c_2}\right)_{T,P,c_1,m}\right]
\end{aligned} \tag{8.25}$$

The two remaining tensors are

$$\begin{aligned}
K_{1\beta\gamma} &= \frac{1}{\det \Theta}\left[c_1\Theta_{22}\left(\frac{\partial \mu_{1p}}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2} - c_2\Theta_{12}\left(\frac{\partial \mu_{2p}}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2}\right] \\
K_{2\beta\gamma} &= \frac{1}{\det \Theta}\left[c_2\Theta_{11}\left(\frac{\partial \mu_{2p}}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2} - c_1\Theta_{21}\left(\frac{\partial \mu_{1p}}{\partial m_{\beta\gamma}}\right)_{T,P,c_1,c_2}\right]
\end{aligned} \tag{8.26}$$

In these expressions, we have used the following notation

$$\det\Theta = \Theta_{11}\Theta_{22} - \Theta_{12}\Theta_{21} \tag{8.27}$$

to denote the determinant of the matrix Θ. The chemical potential expressions per molecular weight for the three components are

$$\begin{aligned}
\rho(\mu_1 - \mu_1^0) &= \varphi + (1 - c_1)\varphi_{c_1} - c_2\varphi_{c_2} - m_{ij}\varphi_{m_{ij}} \\
\rho(\mu_2 - \mu_2^0) &= \varphi + (1 - c_2)\varphi_{c_2} - c_1\varphi_{c_1} - m_{ij}\varphi_{m_{ij}} \\
\rho(\mu_p - \mu_p^0) &= \varphi - c_1\varphi_{c_1} - c_2\varphi_{c_2} - m_{ij}\varphi_{m_{ij}}
\end{aligned} \tag{8.28}$$

μ^0_i are reference constants.

Equations (8.7), in the region of the parameter space $\wp$ in which $\Theta_{ij} >> 1$, become

$$\begin{aligned}
\rho\frac{\partial c_1}{\partial t} &= -\partial_\alpha w_{1\alpha} \\
\rho\frac{\partial c_2}{\partial t} &= -\partial_\alpha w_{2\alpha} \\
w_{1\alpha} &= -\rho D_{11}\partial_\alpha c_1 - \rho D_{12}\partial_\alpha c_2 - \rho K_{1\beta\gamma}\partial_\alpha m_{\beta\gamma} \\
w_{2\alpha} &= -\rho D_{21}\partial_\alpha c_1 - \rho D_{22}\partial_\alpha c_2 - \rho K_{2\beta\gamma}\partial_\alpha m_{\beta\gamma} \\
\frac{\partial m_{\alpha\beta}}{\partial t} &= \partial_\gamma\left(m_{\alpha\beta}\frac{w_{1\gamma}}{\rho c_p}\right) - m_{\gamma\alpha}\partial_\gamma\left(\frac{w_{1\beta}}{\rho c_p}\right) - m_{\gamma\beta}\partial_\gamma\left(\frac{w_{1\alpha}}{\rho c_p}\right) \\
&\quad + \partial_\gamma\left(m_{\alpha\beta}\frac{w_{2\gamma}}{\rho c_p}\right) - m_{\gamma\alpha}\partial_\gamma\left(\frac{w_{2\beta}}{\rho c_p}\right) - m_{\gamma\beta}\partial_\gamma\left(\frac{w_{2\alpha}}{\rho c_p}\right) - 2\lambda m_{\alpha\gamma}m_{\gamma\varepsilon}\varphi_{m_{\varepsilon\beta}}
\end{aligned} \tag{8.29}$$

We notice that the mass flux for each component does not involve the anistropic term $\nabla.\boldsymbol{\sigma}^{(a)}$ as it has been found in Part I (chapter 7). In the absence of flow, the polymer internal deformation produced by the diffusion fluxes is included in the process of mass transport only through the dependence of the internal free energy on $\mathbf{m}$. No anisotropy in diffusion is expected to occur as a consequence of the intrinsic anisotropy of internal

structure deformation. This fact is in a complete agreement with the previous theoretical developments for binary complex mixtures [15-20]. Since, if we ignore c_2 and w_2, i.e. if the second simple fluid component is absent, these equations reduce to the governing equations of the classical non-Fickian model [15-19]. We can therefore regard (8.29) as an extension of the governing equations of the classical non-Fickian models to mixtures involving two solvent components. Finally, we should emphasize that the non-linear reversible part on the right hand side of the last equation in (8.29) is of great importance for system undergoing swelling, but may be dropped if the polymer preserves its volume during diffusion.

8.4.2. m-model

Diffusion of solvents in some polymers (e.g. glassy polymers) creates internal stresses. These stresses are generally localized at the solvents fronts. The propagation of these disturbances can also described by Eqs.(8.29). If Θ_{ij} are large and Max $(1,L_1) \ll R_1$ and Max$(1,L_2) \ll R_2$, then the equation governing the time evolution of $\mathbf{m}$ becomes

$$\frac{\partial m_{\alpha\beta}}{\partial t} = -\partial_\gamma\left(m_{\alpha\beta}N_{\varepsilon\delta}\partial_\gamma m_{\varepsilon\delta}\right) + m_{\gamma\alpha}\partial_\gamma\left(N_{\varepsilon\delta}\partial_\beta m_{\varepsilon\delta}\right) + m_{\gamma\beta}\partial_\gamma\left(N_{\varepsilon\delta}\partial_\alpha m_{\varepsilon\delta}\right) - 2\lambda m_{\alpha\gamma}m_{\gamma\varepsilon}\varphi_{m_{\varepsilon\beta}} \tag{8.30}$$

where $\rho_p = \rho(1-c_1-c_2)$ is the polymer mass density and $(1-c_1-c_2)N = (K_1 + K_2)$. The equation governing the time evolution of ρ_p is

$$\frac{\partial \rho_p}{\partial t} = -\partial_\alpha\left(\rho_p N_{\varepsilon\gamma}\partial_\alpha m_{\varepsilon\gamma}\right) \tag{8.31}$$

The extra stress tensor σ, expressed as a function of $\mathbf{m}$ is given in (8.15). Equations (8.15), (8.30) and (8.31) represent a model of the diffusion of disturbances in the polymeric structure. This model will not be investigated in this paper any further.

8.5. Diffusion without Inertia : (c_1,c_2)-model

We shall now identify regions in the parameter space $\wp$ in which the governing equations can be further simplified. If, in addition to $\Theta_{ij}>>1$, also the relations $L_1<<\min(1, R_1)$ and $L_2 << \min(1, R_2)$ hold, then the coupling between diffusion and the internal structure is weak and can be neglected. Equations (8.29) reduce then to

$$\frac{\partial c_1}{\partial t} = \partial_\alpha\left(D_{11}\partial_\alpha c_1 + D_{12}\partial_\alpha c_2\right)$$

$$\frac{\partial c_2}{\partial t} = \partial_\alpha\left(D_{21}\partial_\alpha c_1 + D_{22}\partial_\alpha c_2\right) \qquad (8.33)$$

where the diffusion coefficients are given in (8.25) in which all terms involving $\mathbf{m}$ are absent. These are the familiar equations governing the generalized Fickian diffusion in a two component mixture of simple fluids [25-26]. In Section 8.7 we shall solve them numerically and compare their solution with experimental observations of a specific pervaporation process.

8.6. Diffusion with w_i-inertia: (c_1,c_2, w_1,w_2) -model

In the regions of the parameter space in which the tensors Θ, L_1 and L_2 are not large, the coupling between the mass fluxes and the internal structure respective governing equations can be ignored. The viscoelastic deformations become irrelevant to the diffusion process and the behavior of the mass transport can be decoupled from the evolution of the internal structure. One may ask in what kind of physical situations such

processes occur? It certainly occurs in the regions of the parameter space in which the tendency towards mixing dominates the elastic resistance brought about by the polymer internal structure. The quantities L_1 and L_2 express the ratio of the elastic free energy to the mixing free energy [27]. The elastic free energy is proportional to the elastic modulus of the polymeric chains and the mixing free energy, following the Flory mean-field theory [27], to the quantity $\frac{kT}{\upsilon}$, where k is Boltzmann's constant, T is the thermodynamic temperature and υ is the cell volume occupied by one monomer. The inequality $L_i << 1$, i=1,2, translates into $\frac{G_0}{\left(kT/\upsilon\right)} << 1$ (in elastomers we have typically $G_0 = 10^6$ Pa, (kT/ν) $\sim 10^7$-10^8 and L ~0.1- 0.01 [28]). In such situation diffusion becomes a process with double inertia, namely the inertia that stems from both w_1 and w_2.

Before studying numerically the implications of Eqs.(8.16), we first investigate the properties of the linear waves that propagate in the polymer as small perturbations.

8.6.1. Travelling waves

In the region of the parameter space in which Θ, L_1 and L_2 are not large, the diffusion process can be described by the following governing equations in which the velocities v_1 and v_2 are used as the state variables instead of the mass fluxes $w_1=\rho c_1 v_1$ and $w_2=\rho c_2 v_2$

$$\frac{\partial c_1}{\partial t} = -c_1 \partial_\alpha v_{1\alpha} - v_{1\alpha} \partial_\alpha c_1$$

$$\frac{\partial c_2}{\partial t} = -c_{21} \partial_\alpha v_{2\alpha} - v_{2\alpha} \partial_\alpha c_2$$

$$\frac{\partial v_{1\gamma}}{\partial t} = -v_{1\beta}\partial_\beta v_{1\gamma} - \frac{1}{\rho}\varphi_{c_1c_1}\partial_\gamma c_1 - \frac{1}{\rho}\varphi_{c_1c_2}\partial_\gamma c_2 - v_{11}v_{1\gamma} - v_{12}v_{2\gamma}$$
$$\frac{\partial v_{2\gamma}}{\partial t} = -v_{2\beta}\partial_\beta v_{2\gamma} - \frac{1}{\rho}\varphi_{c_2c_2}\partial_\gamma c_2 - \frac{1}{\rho}\varphi_{c_2c_1}\partial_\gamma c_1 - v_{21}v_{1\gamma} - v_{22}v_{2\gamma} \qquad (8.34)$$

where we have used the following notation

$$v_{11} = \Theta_{11}, v_{12} = \frac{c_2\Theta_{12}}{c_1}, v_{21} = \frac{c_1\Theta_{21}}{c_2}, \; v_{22} = \Theta_{22}. \qquad (8.35)$$

To discuss solutions of (8.34), it is useful to rewrite (8.34) into the form

$$\frac{\partial U}{\partial t} + \mathbf{A}\nabla U = -\mathbf{B}U \qquad (8.36)$$

where U are the state variables, **A** and **B** are the matrices that arise from identifying (8.36) with (8.34). As many experimental observations (sorption, permeation, pervaporation, etc) are unidirectional, we derive consequences of the Eqs. (8.36) in one the dimensional setting. In this setting, $U = (c_1, v_1, c_2, v_2)^T$ and the matrices **A** and **B** are given by

$$\mathbf{A} = \begin{pmatrix} v_1 & c_1 & 0 & 0 \\ a_{11} & v_1 & a_{12} & 0 \\ 0 & 0 & v_2 & c_2 \\ a_{21} & 0 & a_{22} & v_2 \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & v_{11} & 0 & v_{12} \\ 0 & 0 & 0 & 0 \\ 0 & v_{21} & 0 & v_{22} \end{pmatrix} \qquad (8.37)$$

with

$$\rho a_{11} = \varphi_{c_1c_1},\ \rho a_{12} = \varphi_{c_1c_2},\ \rho a_{21} = \varphi_{c_2c_1},\ \rho a_{22} = \varphi_{c_2c_2} \tag{8.38}$$

$\varphi_{c_ic_j}$ stands for the second derivative of φ with respect to c_i and c_j. In the linear regime, we look for solutions of Eqs.(8.36) in the form $U = U_{eq} + \tilde{U}\exp i(\omega t + kx)$, where $U_{eq} = (c_{1eq}, 0, c_{2eq}, 0)^T$ is the unperturbed solution, (i^2=-1), ω is the frequency of the wave , $k = k_{re} + i\,k_{im}$ is the wave number vector in the propagation direction and x is the direction of propagation of the solution. Notice that $a_{12} = a_{21}$ due to the symmetry property of the Hessian matrix $(\varphi_{c_ic_j})_{1\le i,j\le 2}$. The set of the governing equations (8.34) is time-hyperbolic in the linear regime if the eigenvalues of $A|_{U_{eq}}$ are real. The solutions are moreover stable if the real parts of the eigenvalues of $B|_{U_{eq}}$ are non negative.

The first requirement leads to the following condition

$$\left(c_1\varphi_{c_1c_1} + c_2\varphi_{c_2c_2}\right) \pm \sqrt{\left(c_1\varphi_{c_1c_1} + c_2\varphi_{c_2c_2}\right)^2 - 4c_1c_2\left(\varphi_{c_1c_1}\varphi_{c_2c_2} - \left(\varphi_{c_1c_2}\right)^2\right)} \ge 0 \tag{8.39}$$

that is satisfied if

$$\left(\varphi_{c_1c_1}\varphi_{c_2c_2} - \left(\varphi_{c_1c_2}\right)^2\right) \ge 0 \tag{8.40}$$

The second requirement gives

$$\frac{1}{2}\left[\left(v_{11} + v_{22}\right) \pm \sqrt{\left(v_{11} + v_{22}\right)^2 - 4\left(v_{11}v_{22} - v_{12}v_{21}\right)}\right] \tag{8.41}$$

which is satisfied if

$$(\nu_{11}\nu_{22} - \nu_{12}\nu_{21}) \geq 0 \tag{8.42}$$

Expressions (8.40) and (8.42) constitute then the stability conditions for diffusion described by Eqs.(8.34). The waves obtained as solutions to Eqs.(8.34) are called osmotic waves [20] because they are produced by osmotic means. By inserting the expression of U into (8.36) and keeping only the linear terms in $\tilde{U}$, we arrive at the dispersion relation $k = k(\omega)$

$$P_1\left(\frac{k}{\omega}\right)^4 - 2P_2\left(\frac{k}{\omega}\right)^2 + P_3 = 0 \tag{8.43}$$

where we have used, for simplicity

$$P_1 = \left[c_1 c_2 (a_{11}a_{22} - a_{12}a_{21})\right]_{U=U_{eq}}$$

$$P_2 = \frac{1}{2}\left[c_2 a_{22}\left(1 - \frac{i}{\omega}\nu_{11}\right) + c_1 a_{11}\left(1 - \frac{i}{\omega}\nu_{22}\right) + \left(\frac{i}{\omega}\right)(c_1 a_{21}\nu_{12} + c_2 a_{12}\nu_{21})\right]_{U=U_{eq}}$$

$$P_3 = \left[1 - \frac{1}{\omega^2}(\nu_{11}\nu_{22} - \nu_{12}\nu_{21}) - \left(\frac{i}{\omega}\right)(\nu_{11} + \nu_{22})\right]_{U=U_{eq}} \tag{8.44}$$

Introducing still another notation by

$$\alpha = \frac{P_2}{P_1} = \alpha_1 + i\alpha_2, \quad \beta = \frac{P_3}{P_1} = \beta_1 + i\beta_2 \tag{8.45}$$

and

$$G = 2\alpha_1\alpha_2 - \beta_2 \qquad H = \alpha_1^2 - \alpha_2^2 - \beta_1 \tag{8.46}$$

where

$$\alpha_1 = \frac{1}{2P_1}\left[c_1 a_{11} + c_2 a_{22}\right]_{U=U_{eq}} \tag{8.47}$$

$$\alpha_2 = -\left(\frac{1}{2P_1\omega}\right)\left[c_2a_{22}v_{11} + c_1a_{11}v_{22} - c_1a_{21}v_{12} - c_2a_{12}v_{21}\right]_{U=U_{eq}} \tag{8.48}$$

$$\beta_1 = \frac{1}{P_1}\left[1 - \frac{1}{\omega^2}\left(v_{11}v_{22} - v_{12}v_{21}\right)\right]_{U=U_{eq}} \tag{8.49}$$

$$\beta_2 = -\left(\frac{1}{P_1\omega}\right)\left[\left(v_{11} + v_{22}\right)\right]_{U=U_{eq}} \tag{8.50}$$

the dispersion relation can be written as

$$\left(\frac{k}{\omega}\right)^2 = X + iY \tag{8.51}$$

This leads the following expression for the phase velocity

$$v_{ph} = \sqrt{\frac{2}{X^{\pm} + \sqrt{\left(X^{\pm}\right)^2 + \left(Y^{\pm}\right)^2}}} \tag{8.52}$$

and for the intensity of attenuation

$$a(\omega) = -2k_{im} = -\omega Y^{\pm} v_{ph} \tag{8.53}$$

where

$$X^{\pm} = \alpha_1 \pm \sqrt{\frac{H + \sqrt{H^2 + G^2}}{2}} \tag{8.54}$$

$$Y^{\pm} = \alpha_2 \pm \frac{G}{\sqrt{2\left(H + \sqrt{H^2 + G^2}\right)}} \tag{8.55}$$

In the high frequency limit, $\omega \to \infty$, we find, in view of (8.44)-(8.55), that the phase velocity reduces to

$$v_{ph}^{\pm} \approx \frac{1}{\sqrt{\alpha_1 \pm \sqrt{\alpha_1^2 - 1/P_1}}} \tag{8.56}$$

We thus see that in the high frequency limit Eqs.(8.34) predict the propagation of two types of waves, both having constant velocities (frequency independent), namely v_{ph}^{+} and v_{ph}^{-} given by (8.56).

The attenuation, on the other hand, becomes

$$a(\omega) \approx v_{ph}^{\pm}\left(\frac{\tilde{\alpha}_2}{2P_1} \pm \frac{\alpha_1\tilde{\alpha}_2 - \tilde{\beta}_2}{2P_1\sqrt{\alpha_1^2 - 1/P_1}}\right) \tag{8.57}$$

where we have used the notation

$$\tilde{\alpha}_2 = \left[c_2a_{22}v_{11} + c_1a_{11}v_{22} - c_1a_{21}v_{12} - c_2a_{12}v_{21}\right]_{U=U_{eq}}$$

$$\tilde{\beta}_1 = \left[(v_{11}v_{22} - v_{12}v_{21})\right]_{U=U_{eq}}$$

$$\tilde{\beta}_2 = \left[(v_{11} + v_{22})\right]_{U=U_{eq}} \tag{8.58}$$

In the low frequencies limit $\omega \to 0$, the phase velocity is

$$v_{ph}^{\pm}(\omega) \approx \sqrt{\frac{2\omega}{\left(\frac{\tilde{\alpha}_2}{2P_1} \mp \sqrt{\left(\frac{\tilde{\alpha}_2}{2P_1}\right)^2 - \frac{\tilde{\beta}_1}{P_1}}\right)}} \tag{8.59}$$

and the intensity attenuation is determined as

$$a^{\pm}(\omega) \approx \sqrt{2\left(\frac{\tilde{\alpha}_2}{2P_1} \mp \sqrt{\left(\frac{\tilde{\alpha}_2}{2P_1}\right)^2 - \frac{\tilde{\beta}_1}{P_1}}\right)}\omega \qquad (8.60)$$

We thus see that in the low frequency limit both the phase velocity and the attenuation tend to zero.

Notice that if $c_2 = 0$ (or $c_1 = 0$), we recover the result derived in case of binary mixtures [19-20].

8.6.2. Material Coordinates

The rearrangements in the polymer that are needed to accommodate the solvents produce its swelling. This deformation is associated with a change of the volume of the polymer and thus leads to a change of its boundaries. Under this volume non-preserved condition, it becomes difficult to formulate appropriately the boundary conditions due to their time change. To overcome this difficulty, we shall follow [17] and reformulate the governing equations of the diffusion in the material (also called Lagrangian) coordinates. The material coordinates will be denoted by the symbol **Y**. We recall that the spatial (also called Eulerian) coordinates are denoted in this paper by **r**. the deformation matrix is

$$F^{-1}_{\alpha\beta} = \frac{\partial Y_\alpha}{\partial r_\beta} \qquad (8.61)$$

In the regions of the parameter space where L_{1ij} and L_{2ij} are not large, and by applying the one-to-one transformation $\mathbf{r} \rightarrow \mathbf{Y}$ to Eq. (8.16) we obtain

$$\rho \frac{\partial c_1}{\partial t} = -F^{-1}_{\alpha\beta} \nabla_\beta w_{1\alpha}$$

$$\rho\frac{\partial c_2}{\partial t} = -F_{\alpha\beta}^{-1}\nabla_\beta w_{2\alpha}$$

$$\frac{\partial w_{1\gamma}}{\partial t} = -F_{\beta\delta}^{-1}\nabla_\delta\left(w_{1\gamma}\frac{w_{1\beta}}{\rho c_1}\right) - \Theta_{11}\left(w_{1\gamma}+\overline{Q}_{1\gamma}\right) - \Theta_{12}\left(w_{2\gamma}+\overline{Q}_{2\gamma}\right)$$

$$\frac{\partial w_{2\gamma}}{\partial t} = -F_{\beta\delta}^{-1}\nabla_\delta\left(w_{2\gamma}\frac{w_{2\beta}}{\rho c_2}\right) - \Theta_{21}\left(w_{1\gamma}+\overline{Q}_{1\gamma}\right) - \Theta_{22}\left(w_{2\gamma}+\overline{Q}_{2\gamma}\right) \qquad (8.62)$$

where we have rearranged appropriately Eqs.(8.16) to make arise in them the following expressions

$$\overline{Q}_{1\alpha} = -\rho D_{11}F_{\alpha\beta}^{-1}\nabla_\beta c_1 - \rho D_{12}F_{\alpha\beta}^{-1}\nabla_\beta c_2$$

$$\overline{Q}_{2\alpha} = -\rho D_{21}F_{\alpha\beta}^{-1}\nabla_\beta c_1 - \rho D_{22}F_{\alpha\beta}^{-1}\nabla_\beta c_2 \qquad (8.63)$$

which stand for the generalized Fick's laws for ternary mixtures [24-26]. Θ_{ij} and D_{ij} are the phenomenological parameters of the model and may be chosen as dependent functions on the mass fractions of the two solvents. The couplings occurring between diffusion in the Equations (8.62) are of two types: a strong coupling and a weak coupling. The former is brought about, in the mass flux equation of each component j, by the term $\Theta_{jj}(w_j + \overline{Q}_j)$ which contains the gradient of the concentration of the other component i. The weak coupling comes from the cross coupling expressions: $\Theta_{ij}(w_j + \overline{Q}_j)$. If $\Theta_{12} \ll 1$ and $\Theta_{21} \ll 1$, then the weak coupling becomes negligible, but the diffusion equations still remain strongly coupled. If, on the other hand, Θ_{jj} (j=1,2) are very small, only the weak coupling is significant. Such a case is not, however, expected in practical situations.

8.6.4. Dimensionless Formulation

We proceed now to the dimensionless formulation. For the space and time coordinates, we use the following dimensionless quantities

$$\nabla_\alpha = \frac{1}{L_0}\bar{\nabla}_\alpha$$

$$\frac{\partial}{\partial t} = \frac{1}{\tau_{d11}}\frac{\partial}{\partial \theta} \tag{8.64}$$

L_o is a characteristic length scale and $\tau_{d11} = \frac{L_o^2}{D_{11}^*}$ is a characteristic diffusion time scale. $D_{11}^* = D_{11}(c_1 = 0, c_2 = 0)$ is the main diffusion coefficient at infinite dilution. For the mass fractions and mass fluxes (or velocities), we use

$$C_i = \frac{c_i}{c_{1eq}}$$

$$W_i = \left(\frac{\tau_{d11}}{\rho c_{1eq} L_o}\right) w_i, \quad V_i = \left(\frac{\tau_{d11}}{L_o}\right) v_i \quad i = 1,2. \tag{8.64}$$

c_i is the mass fraction of the component i and c_{1eq} is the equilibrium concentration of the component 1 chosen here to be the normalization reference. The dimensionless governing equations in the material coordinates are

$$\frac{\partial C_1}{\partial \theta} = -F_{\alpha\beta}^{-1}\bar{\nabla}_\beta W_{1\alpha}$$

$$\frac{\partial C_2}{\partial \theta} = -F_{\alpha\beta}^{-1}\bar{\nabla}_\beta W_{2\alpha}$$

$$\frac{\partial W_{1\alpha}}{\partial \theta} = -F_{\beta\delta}^{-1}\overline{\nabla}_{\delta}\left(\frac{W_{1\alpha}W_{1\beta}}{C_1}\right) - \frac{1}{De_{11}}\left[W_{1\alpha} + \tilde{D}_{11}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_1 + \tilde{D}_{12}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_2\right]$$
$$- \frac{1}{De_{12}}\left[W_{2\alpha} + \left(\frac{\tau_{d11}}{\tau_{d22}}\right)\tilde{D}_{21}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_1 + \left(\frac{\tau_{d11}}{\tau_{d22}}\right)\tilde{D}_{22}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_2\right]$$

$$\frac{\partial W_{2\alpha}}{\partial \theta} = -F_{\beta\delta}^{-1}\overline{\nabla}_{\delta}\left(\frac{W_{2\alpha}W_{2\beta}}{C_2}\right) - \frac{1}{De_{21}}\left(\frac{\tau_{d11}}{\tau_{d22}}\right)\left[W_{1\alpha} + \tilde{D}_{11}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_1 + \tilde{D}_{12}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_2\right] \quad (8.66)$$
$$- \frac{1}{De_{22}}\left(\frac{\tau_{d11}}{\tau_{d22}}\right)\left[W_{2\alpha} + \left(\frac{\tau_{d11}}{\tau_{d22}}\right)\tilde{D}_{21}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_1 + \left(\frac{\tau_{d11}}{\tau_{d22}}\right)\tilde{D}_{22}F_{\alpha\beta}^{-1}\overline{\nabla}_{\beta}C_2\right]$$

In the third and fourth equations, a Deborah matrix **De**, depending on the solvents concentration, arises (replacing one Deborah number that arises in the mass flux governing equation [20, 29] in binary mixtures) :

$$\mathbf{De} = \begin{pmatrix} De_{11} & De_{12} \\ De_{21} & De_{22} \end{pmatrix} \quad (8.67)$$

Its coefficients are defined as

$$De_{1i}(c_1, c_2) = \frac{1}{\Theta_{1i}(c_1, c_2)\tau_{d11}}$$

$$De_{2i}(c_1, c_2) = \frac{1}{\Theta_{2i}(c_1, c_2)\tau_{d22}} \quad (8.68)$$

for i=1, 2 respectively. Θ_{ij} have been introduced above and τ_{dii} (i=1, 2) are the diffusion characteristic time scale coefficients given by

$$\tau_{dii} = \frac{L_o^2}{D_{ii}^*} \tag{8.69}$$

where $D_{ii}^* = D_{ii}(c_1 \to 0, c_2 \to 0)$. The third and the fourth equation in (8.66) also involve four functions. They are defined as

$$\tilde{D}_{1i}(c_1, c_2) = \frac{D_{1i}(c_1, c_2)}{D_{11}^*}$$

$$\tilde{D}_{2i}(c_1, c_2) = \frac{D_{2i}(c_1, c_2)}{D_{22}^*} \tag{8.70}$$

The Deborah matrix $\mathbf{De}(c_i)$ and the diffusion matrix $\mathbf{D}(c_i)$ are the two phenomenological matrices in which the individual features of the system under consideration are expressed. By letting these parameters depend on the concentrations, we also introduce indirectly the influence of the internal structure deformations on diffusion. This phenomenological description is however less complete than the more microscopic description provided by (8.7) or (8.16) in which the evolution of the internal structure described by the symmetric tensor $\mathbf{m}$ is taken into account. This will be the subject of a future investigation.

In view of the expressions (8.25), we have at infinite dilution

$$\lim_{c_1 \to 0} \lim_{c_2 \to 0} D_{11} = \lim_{c_1 \to 0} \lim_{c_2 \to 0} \left(\frac{RT}{\xi_{1p}} \right) = M_1 D_{10}$$

$$\lim_{c_1 \to 0} \lim_{c_2 \to 0} D_{22} = \lim_{c_1 \to 0} \lim_{c_2 \to 0} \left(\frac{RT}{\xi_{2p}} \right) = M_2 D_{20}$$

$$\lim_{c_1 \to 0} \lim_{c_2 \to 0} D_{12} = 0$$

$$\lim_{c_1\to 0}\lim_{c_2\to 0} D_{21} = 0 \tag{8.71}$$

The main diffusion coefficients D_{11} and D_{22} coincide with the self-diffusion coefficients of the solvents 1 and 2, respectively in their binary mixtures. The cross diffusion coefficients, on the other hand, are equal to zero. Similarly, we find that the coefficients of the inverse of the relaxation matrix are

$$\lim_{c_1\to 0}\lim_{c_2\to 0} \Theta_{11} = \xi_{1p0} = \frac{RT}{M_1 D_{10}} \qquad \lim_{c_1\to 0}\lim_{c_2\to 0} \Theta_{22} = \xi_{2p0} = \frac{RT}{M_2 D_{20}}$$

$$\lim_{c_1\to 0}\lim_{c_2\to 0} \Theta_{12} = 0 \qquad \lim_{c_1\to 0}\lim_{c_2\to 0} \Theta_{21} = 0 \tag{8.72}$$

Evaluation of D_{ij}

In the regions of the parameter space where Θ_{ij} are very large, the diffusion coefficient expressions are found to be functions of Θ_{ij} and thus are dependent on the friction coefficients ξ_{ij}. Consequently, they are expressible in terms of the self-diffusion coefficients of each component in binary mixtures. Assuming that the self-diffusion coefficients of the solvent 1 and of the solvent 2 in the solvent 1-solvent 2 mixture are larger than the diffusion coefficients D_1 and D_2 of the solvent i (i=1,2) in the solvent i-polymer mixtures, the calculated expression for the diffusion coefficients D_{ij} provided by (8.25) simplify considerably.

$$D_{11} = \frac{D_1}{RTc_p}\left[M_1 c_1(1-c_1)\left(\frac{\partial \mu_{1p}}{\partial c_1}\right)_{T,P,c_2,m} - M_2 c_2 c_1\left(\frac{D_2}{D_1}\right)\left(\frac{\partial \mu_{2p}}{\partial c_1}\right)_{T,P,c_2,m}\right]$$

$$D_{12} = \frac{D_1}{RTc_p}\left[M_1 c_1(1-c_1)\left(\frac{\partial \mu_{1p}}{\partial c_2}\right)_{T,P,c_1,m} - M_2 c_1 c_2\left(\frac{D_2}{D_1}\right)\left(\frac{\partial \mu_{2p}}{\partial c_2}\right)_{T,P,c_1,m}\right]$$

$$D_{21}=\frac{D_2}{RTc_p}\left[M_2c_2(1-c_2)\left(\frac{\partial\mu_{2p}}{\partial c_1}\right)_{T,P,c_2,m}-M_1c_1c_2\left(\frac{D_1}{D_2}\right)\left(\frac{\partial\mu_{1p}}{\partial c_1}\right)_{T,P,c_2,m}\right]$$

$$D_{22}=\frac{D_2}{RTc_p}\left[M_2c_2(1-c_2)\left(\frac{\partial\mu_{2p}}{\partial c_2}\right)_{T,P,c_1,m}-M_1c_1c_2\left(\frac{D_1}{D_2}\right)\left(\frac{\partial\mu_{1p}}{\partial c_2}\right)_{T,P,c_1,m}\right] \qquad (8.73)$$

D_i , i=1,2, depends on the concentrations of the solvents. The expressions that have been already proposed in [6-8] are

$$D_1=D_{10}\exp(n_1c_1+m_1c_2)$$
$$D_2=D_{20}\exp(n_2c_1+m_2c_2) \qquad (8.74)$$

where n_i and m_i are material constants (also called plasticizing constants), D_{10} and D_{20} are the diffusion coefficients at infinite dilution.

8.6.5. 1D Numerical Analysis

In this subsection we investigate numerically two interesting cases : i) a pervaporation process by a rubbery polymer, and ii) a sorption process in a glassy polymer. First, we investigate the pervaporation process of toluene-benzene binary mixture by the poly(ethylene terephthalate) membrane and compare the calculated results with results of experimental measurements. We have in mind the experiment carried out in[7]. Second, we study the sorption of a binary mixture through a glassy polymer. The behavior of the first pure component (methyl chloride) is Fickean and the behavior of the second pure fluid (benzene) is Case II. The sorption process of their mixture shows (by varying the composition of the mixture in feed) a continuous transition from Case II to the Fickian mass transport [12].

Pervaporation [6-10] and sorption [12] experiments are usually based on the use of a thin polymer membrane. As this process is unidirectional, we limit the numerical investigation to the one dimensional study. Let Z be the space coordinate across the membrane. Following earlier works [17], the deformation matrix in this one dimensional description can be expressed as a function of the polymer volume fraction

$$F_{11} = \frac{1}{\phi_p} \tag{8.75}$$

where $\phi_p = 1 - \phi_1 - \phi_2$. ϕ_i (i=1, 2) is the volume fraction of the component i. It is related to the mass fraction as $\gamma_i \phi_i = \rho c_i$, γ_i is the material density (assumed to be constant), ρ is the global mass density (also assumed to be constant) and c_i is the mass fraction.

8.6.5.a. Pervaporation : Generalized Fickian diffusion $D_{cij} >> 1$

Most membranes used for the separation process between two components are rubber (elastomers). In these polymers, the time scale of the response of the polymeric chains is greater than the characteristic time scales of the penetration process. Therefore, the pervaporation behaviors clearly situate in the regions of the parameter space characterized by the constraints $D_{cij} >> 1$ and for which we have already arrived at the governing equations in Section IV. In the one dimensional setting, these dimensionless equations are as follows

$$\frac{\partial C_1}{\partial \theta} = F_{11}^{-1} \frac{\partial}{\partial Z}\left(\tilde{D}_{11} F_{11}^{-1} \frac{\partial C_1}{\partial Z} + \tilde{D}_{12} F_{11}^{-1} \frac{\partial C_2}{\partial Z} \right)$$

$$\frac{\partial C_2}{\partial \theta} = \left(\frac{\tau_{d11}}{\tau_{d22}} \right) F_{11}^{-1} \frac{\partial}{\partial Z}\left(\tilde{D}_{21} F_{11}^{-1} \frac{\partial C_1}{\partial Z} + \tilde{D}_{22} F_{11}^{-1} \frac{\partial C_2}{\partial Z} \right) \tag{8.76}$$

Using Eqs. (8.76), we investigate particularly the pervaporation of the toluene-benzene mixture by a poly (ethylene terephthalate) (PET) membrane. The calculated results are compared with the experimental observations reported in[7]. The membrane has a thickness of 3.5 micrometer and a degree of crystallinity of 2%. At the experiment temperature (30 °C), PET can be assumed to be closed to its rubbery state . This then means that Eqs. (8.76) constitute a good approximation for describing the observations. The diffusion coefficients at the infinite dilution are $D^{10}=1.2\ 10^{-14}$ (m^2/sec) and $D^{20}=1.4\ 10^{-14}$ (m^2/sec) for toluene and benzene respectively [7]. We emphasize that the diffusion coefficients arising in Eqs. (8.76) are obtained as a consequence of the model which is derived in the absence of the overall flow. The measurements, however, are generally carried out in the volume frame of reference. We have to correct then D^{10} and D^{20} (to obtain the appropriate self-diffusion coefficients to be applied in the Eqs.(8.76)) by the multiplication constant (ρ/ρ_p) such that $D^{i0} = (\rho/\rho_p)D_{i0}$ [25,26] where ρ is the overall mass density of the binary solvent-polymer mixture and mass density of the polymer chosen here to be of 1.18 g/cm^3 at 30 °C. D_{i0} is then the value used in the calculations. We also use as in [6-8] their obtained values for the plasticizing constants (II.74) $n_1= n_2 = 139.4$ and $m_1= m_2=212.77$.

All the physical quantities needed to solve numerically Eqs (8.76) are now specified above. We proceed to discuss the initial and the boundary conditions. In the pervaporation experiments, a dense membrane is used to separate two components composing a binary mixture. The permeate has a different composition than the mixture in the feed. A vacuum is required in the downstream part to ensure a permanent gradient of the chemical potential (or gradient of pressure). Consequently, one can use the following initial and boundary conditions

$$C_1(Z,\theta=0)=0 \qquad C_2(Z,\theta=0)=0$$

$$C_1(Z=0,\theta)=1 \qquad C_2(Z=0,\theta)=\frac{C_{2eq}}{C_{1eq}}$$

$$C_1(Z=1,\theta)=0 \qquad C_2(Z=1,\theta)=0 \qquad (8.77)$$

Figure 8.1 shows the equilibrium mass fractions for toluene drawn in (▲) and for benzene drawn in (●) versus the mass fraction of toluene in the feed. These values are calculated based on the experimental data reported in [7] at 30 °C. As shown in Figure 8.1, the equilibrium mass fractions of the two components are very small compared with unity and the deformation gradient F_{11} is of the order of unit, i.e. the membrane swelling in this situation can be regarded as negligible. The interaction parameters[7] are χ_{12}=0, χ_{1p}=5.57 χ_{2p} = 5.52, where the indices 1, 2 and p designate toluene, benzene and PET respectively. The steady permeation flux values for toluene and benzene versus the mass fraction of toluene in feed are given in Figure 8.2. A relatively good agreement between the experimental data drawn in (▲) for toluene and (●) for benzene and the calculated curves (drawn in continuous lines). A discrepancy, is however, detected at the toluene mass fraction in feed of 0.7. The same deviation from the general line (See Figure 8.1) is also observed for the experimental equilibrium density. The latter constitutes one of the relevant parameters that influences significantly the behavior of diffusion. The Flory-Huggins [27] expression for the mixing free energy is used to assess the diffusion coefficients. The diffusion matrix which is concentration dependent and the permeation fluxes are calculated at each time step. The unsteady permeation fluxes for toluene and benzene versus time are shown in Figure 8.3 and Figure 8.4 respectively for different mass fraction of toluene in the feed.

8.6.5.b Sorption of solvent-solvent mixtures into a glassy polymer : Case II - Fickian transition

The experimental situation in which we are interested in this subsection is the sorption of a mixture of two simple components in a thin film of glassy polymer. The diffusion behavior of the first component, 1, in its pure state, is Fickean. The second pure component, 2, exhibits on the other hand the Case II diffusion. The behavior of their

mixture varies then from the Fickean to the Case II upon changing the composition of the binary mixture in the feed. As an illustration, we mention the observation reported in [12]. In these experiments, a glassy epoxy resin was used as the polymer film, pure Benzene follows the Case II behavior, and the pure methyl chloride exhibits Fickian diffusion. One observes, by changing the composition of the mixture, that the mixture shows a series of intermediate behaviors ranging from these two extreme cases. It is well known that some solvents diffuse into glassy polymers following the Case II behavior while other solvents exhibit the Fickean character in the same polymers. This may be related among others to the physical properties of the solvent and the polymer and more importantly to the affinities (interaction) that develop between them. For example methanol shows the Case II behavior in the poly(methyl methacrylate) [2], but diffuses in a Fickian way in polystyrene. In order to fully understand these effects, the model has to be developed on the molecular level of description. The model introduced in this paper cannot explain the phenomena but it can describe them if experimentally measured parameters (diffusion coefficients, relaxation times etc.) are put into it.

To simplify our considerations, we shall assume that the coupling between the mass fluxes governing equations are negligible, i.e. $De_{12} >> 1$ and $De_{21} >> 1$. As diffusion of the component 1 (methyl chloride) is Fickean, De_{11} becomes very small. Because the penetration behavior of the component 2 (benzene) is of Case II type, De_{11} is greater than unity. Since, in this case, the relaxation time scale of the mass flux is larger than the characteristic time scale of diffusion. Consequently, the inertial effects become so significant to influence the behavior of diffusion. The governing equations (8.66) corresponding to this particular situation simplify to

$$\frac{\partial C_1}{\partial \theta} = F_{11}^{-1} \frac{\partial}{\partial Z}\left(\tilde{D}_{11} F_{11}^{-1} \frac{\partial C_1}{\partial Z} + \tilde{D}_{12} F_{11}^{-1} \frac{\partial C_2}{\partial Z} \right)$$

$$\frac{\partial C_2}{\partial \theta} = -F_{11}^{-1}\left(\frac{\partial W_2}{\partial Z} \right)$$

$$\frac{\partial W_2}{\partial \theta} = -F_{11}^{-1}\frac{\partial}{\partial Z}\left(\frac{W_2 W_2}{C_2}\right) - \frac{1}{De_{22}}\left(\frac{\tau_{d11}}{\tau_{d22}}\right)\left[W_2 + \left(\frac{\tau_{d11}}{\tau_{d22}}\right)\tilde{D}_{21}F_{11}^{-1}\frac{\partial C_1}{\partial Z} + \left(\frac{\tau_{d11}}{\tau_{d22}}\right)\tilde{D}_{22}F_{11}^{-1}\frac{\partial C_2}{\partial Z}\right]$$

(8.78)

Now, we turn our attention to the initial and boundary conditions. We shall assume that the initial thickness of the sample, $2L_0$, is negligible in comparison with the surface, S, of the film, i.e. $2L_0 << \sqrt{S}$. The process of sorption into a thin film is a symmetric process; i.e., the solvent enters the polymer from opposite sides and diffuses to the center of the film. We can therefore study only the half-thickness of length L_0.

The initial conditions are:

$$C_1(Z, 0) = 0$$
$$C_2(Z, 0) = 0$$
$$W_2(Z, 0) = 0 \qquad (8.79)$$

The boundary conditions are:

$$C_1(Z = 0,\theta) = 1 \qquad \left.\frac{\partial C_1}{\partial Z}\right|_{Z=1} = 0$$

$$C_2(Z = 0,\theta) = \frac{c_{2eq}}{c_{1eq}} \qquad W_2(Z = 0, \Theta = 0) = \left(\frac{c_{2eq}}{c_{1eq}}\right)\left(\frac{\tau_{d11}}{\tau_{d22}}\right) \qquad (8.80)$$

In view of (8.80) the third equation, at the polymer-solvent interface, becomes

$$\left.\frac{\partial W_{2\alpha}}{\partial \theta}\right|_{Z=0} = -\left(\frac{\tau_{d11}}{\tau_{d22}}\right)\left(\frac{W_{2\alpha}(0,\theta)}{De_{22eq}}\right) \qquad (8.81)$$

which expresses the relaxation of the mass flux for the component 2.

In the governing equations, only De_{22} constitutes the fitting parameter of the model. We have chosen it to be De_{22}=1000 to get the Case II diffusion for the component 2 at the pure state. De_{22} is fixed by the complete time of penetration of the pure component into the film. Figure 8.5 shows the mass uptake versus time for different compositions in the mixture feed. We see clearly the Case II-Fickean transition during the sorption process when one goes from the pure fluid 2 to the pure Fickean fluid 1. The same behavior has been observed in [12]. The mass uptake in case of the pure benzene (c_0 =1 in the feed) varies linearly with time with a constant velocity. For the pure methyl chloride fluid, the mass uptake varies as a square root of time as shown by the curve (c_0=0). Between these extreme cases, the behavior of the mass uptake follows an intermediate behavior that can be described by $M = k_1\sqrt{t} + k_2 t$, where k_1 and k_2 are given constants[12].

Figures 8.6, 8.7, 8.8, 8.9 and 8.10 show respectively the concentration profiles of the mixtures for the following compositions (benzene/methyl chlorides) = (1/0), (0.8/0.2), (0.5/0.5), (0.3/0.7) and (0/1). Figure 8.6 shows a behavior typical of Case II diffusion the concentration profiles are step like and there is almost no gradients of the concentration behind the front. Figure 8.10 on the other hand exhibits the well known Fickian behavior.

8.7. Conclusion

In this paper, we have introduced a new model for the isothermal diffusion of a binary simple fluids (e.g. solvents, etc.) in a complex fluid (e.g. a polymer) under the conditions of the global incompressibility and the absence of the overall flow. The state variables used to describe the diffusion processes (occurring in complex ternary mixtures) are the mass fractions c_1 and c_2 and diffusion mass fluxes $\mathbf{w}_1$ and $\mathbf{w}_2$ of the two simple fluids, and a symmetric second order tensor $\mathbf{m}$ accounting for the internal structure of the polymer. The governing equations (8.7)-(8.20), in which diffusion and deformation are mutually coupled, constitute the main results of this paper. In this model,

all the individual features of the binary-solvents-polymer mixture are expressed in the free energy, the matrix relaxation time inverse Θ of the diffusion fluxes and the relaxation time inverse λ of the internal structure.

Diffusion in ternary mixtures that is described by Equations (8.7)-(8.20) can be regarded as a process with triple inertia. In the process of looking at the solutions of the governing equations, we have investigated them asymptotically in a systematic and pedagogic manner. We arrived at simpler models in which some of the state variables become irrelevant to describing particular behavior of diffusion. Three situations were discussed thoroughly:

(i) Diffusion with a single inertia (m-inertia) described by Eqs. (8.29)

(ii) Diffusion without inertia described by Eqs. (8.33)

(iii) Diffusion with double inertia ((w_1, w_2)-inertia) described in Section 8.6.

In (i) the equations (8.29) extend, to ternary mixtures, the governing equations of the classical Case II models derived previously for binary mixtures [15-20]. As an outcome of the model, we have also provided explicit expressions for the transport coefficients (8.24)-(8.26) in terms of the relaxation matrix Θ. Using the molecular results of Bearman [23], we were also able to express the coefficients of Θ in terms of the friction coefficients.

In (ii) the inertial variables (w_1, w_2, m) are assumed to evolve faster than the mass transport. In this situation, described by the governing equations (8.33), the model involves cross coupling terms in the mass fluxes and thus renders the description more complex than the Fickian one. Numerical results for these equations are provided and compared with a chosen experimental measurements of a pervaporation process [8] of a binary mixture by a thin membrane. A rather good agreement has been found between the calculated profiles and the measured data.

In (iii) the inertia of the state variable m describing the viscoelastic deformations of the polymer internal structure is ignored. Such a situation occurs when the mixing part of the free energy dominates the elastic part. In this case, the concentration of each component evolves with double inertia due to the cross couplings arising between the diffusion fluxes. In the way of investigating solutions to this reduced model, we have first

discussed analytically the propagation of waves in ternary mixtures and have calculated their phase velocities and their intensity attenuation formulas. For example, we find out that in the domain of large frequencies, two waves propagate with constant velocities that are frequency independent. In the domain of small frequencies, both the phase velocities and the attenuation are proportional to the square root of the frequency. An experimental investigation of the diffusion waves may turn out to become a new and useful way to study experimentally the non-Fickian diffusion processes. Second, we look at the implications of this model for describing more complex situations that occur, for instance, in glassy polymers. We recall that the governing equations (8.62) are a direct generalization of the governing equations derived in a previous model[20] for binary mixtures, and for which they have been used to recover, in a simple manner, the Case II behavior. A numerical solution of these equations for the sorption process of a binary mixture in a glassy polymer is provided.

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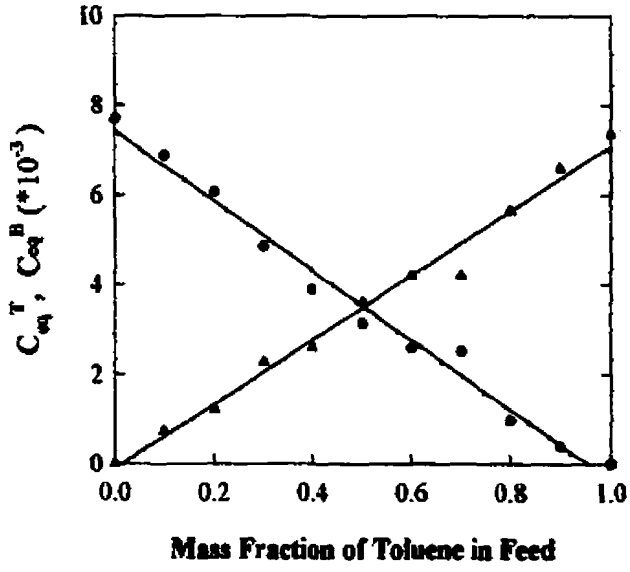

Figure 8.1. Equilibrium mass fractions of toluene (▲) and benzene (●) against the mass fraction of toluene in the mixture feed

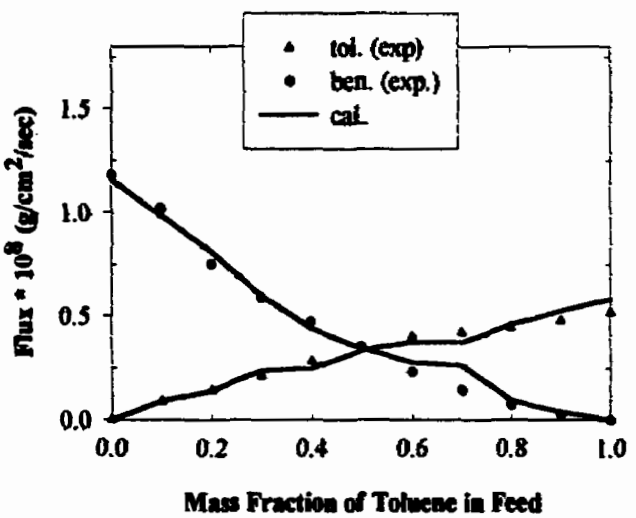

Figure 8.2 Permeation rates of toluene (▲) and benzene (●) against the mass fraction of toluene in the mixture feed at 30 °C

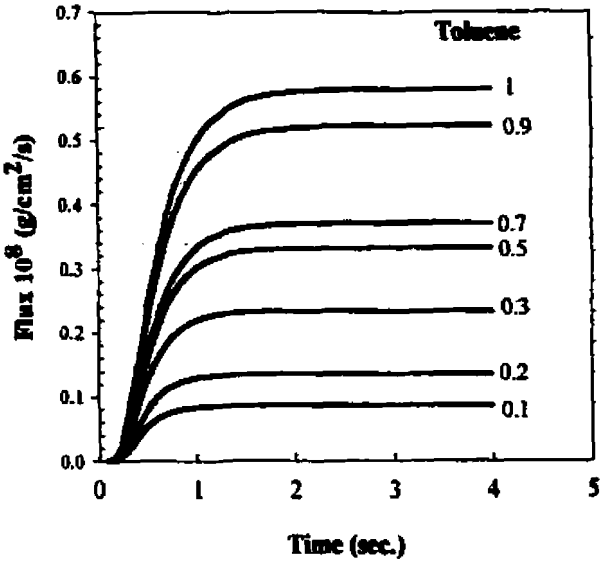

Figure 8.3. Permeation rates of toluene versus time for various compositions of mixtures. Numbers denote the mass fraction of toluene in the feed.

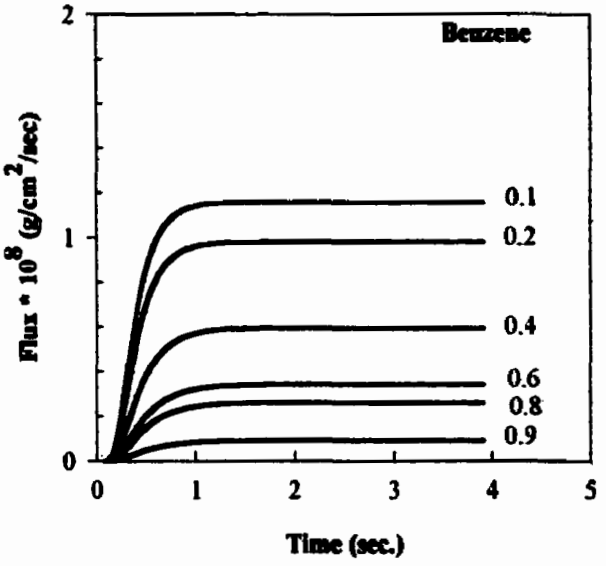

Figure 8.4. Permeation rates of benzene versus time for various compositions of mixtures. Numbers denote the mass fraction of toluene in the feed.

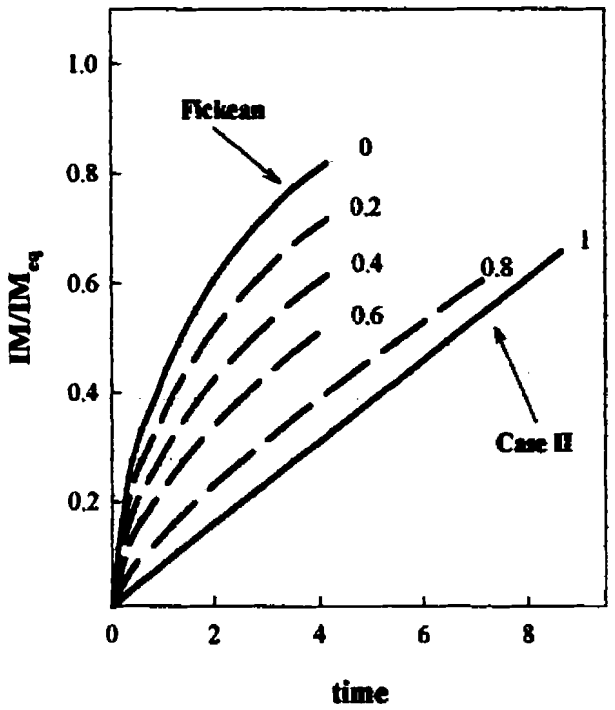

Figure 8.5: Normalized mass uptake of polymer in the benzene-methyl chloride mixtures for various compositions versus normalized time. Numbers designate the mass fraction of benzene in the feed.

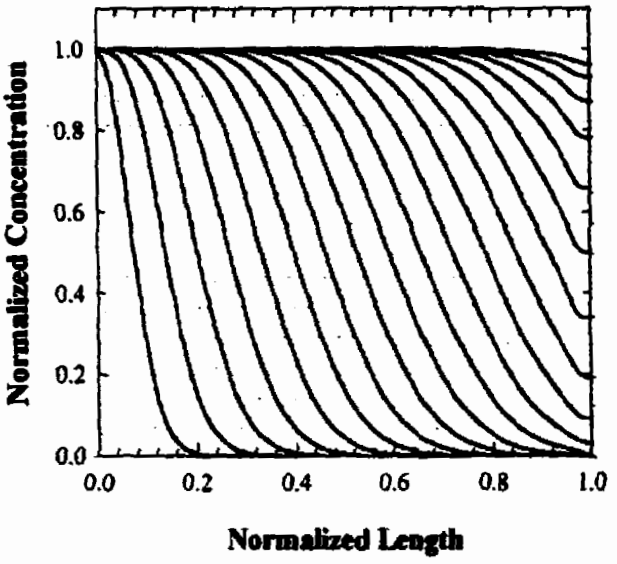

Figure 8.6: Normalized concentration profiles versus the normalized half thickness of the polymer for the composition of (benzene/methyl chloride)=(1/0) in the mixture feed.

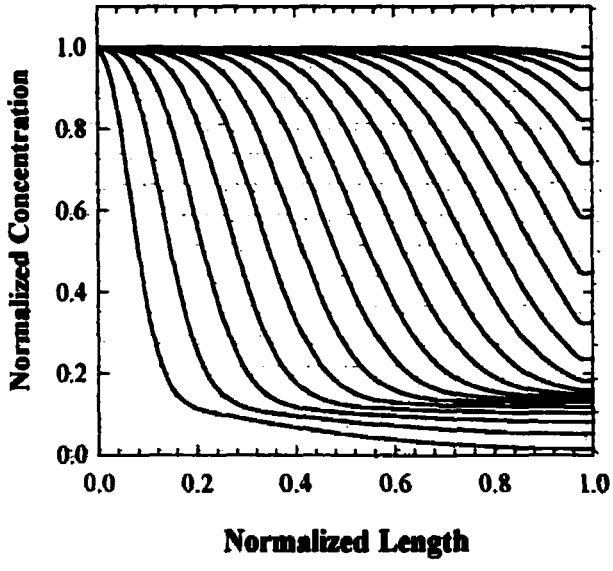

Figure 8.7: Normalized concentration profiles versus the normalized half thickness of the polymer for the composition of (benzene/methyl chloride)=(0.8/0.2) in the mixture feed.

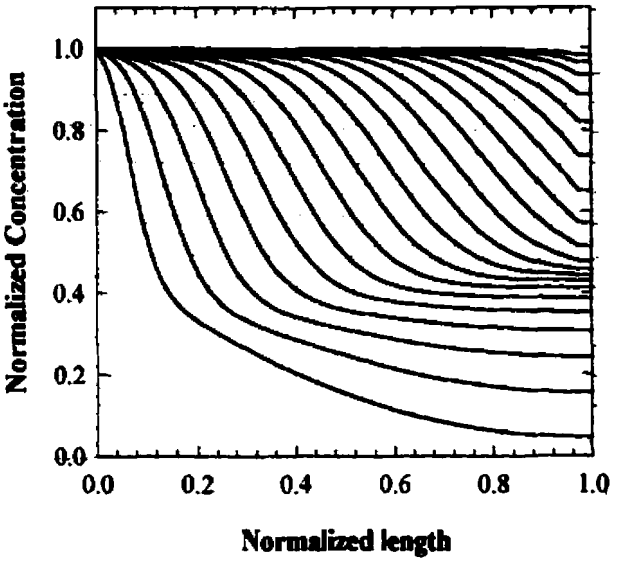

Figure 8.8: Normalized concentration profiles versus the normalized half thickness of the polymer for the composition of (benzene/methyl chloride)=(0.5/0.5) in the mixture feed.

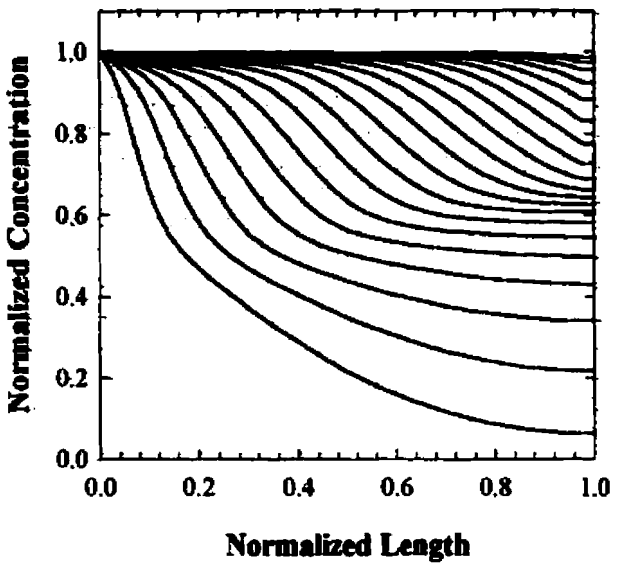

Figure 8.9: Normalized concentration profiles versus the normalized half thickness of the polymer for the composition of (benzene/methyl chloride)=(0.3/0.7) in the mixture feed.

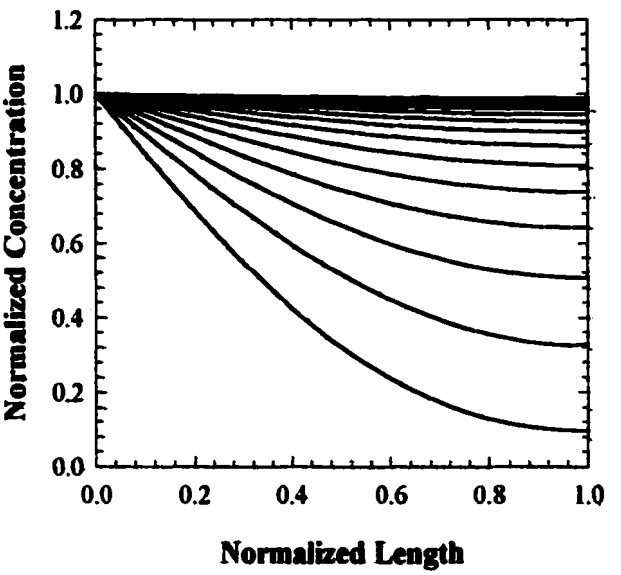

Figure 8.10: Normalized concentration profiles versus the normalized half thickness of the polymer for the composition of (benzene/methyl chloride)=(0/1) in the mixture feed.

Chapitre 9 Conclusions Générales

Le travail de cette thèse porte sur l'étude des comportements non-Fickiens du transfert de masse qui sont observés dans les mélanges solvant-polymère soumis ou non à un écoulement imposé. Ces comportements résultent des couplages qui surviennent entre la diffusion, l'écoulement et la déformation de la structure interne du polymère. L'une des raisons principales menant à de telles observations est liée aux caractères de l'individualité et de la non linéarité de la microstructure qui, essentiellement, déterminent et définissent les propriétés physico-chimiques des polymères.

La stratégie générale que nous avons poursuivie pour comprendre ces phénomènes se réalise par une modélisation en deux étapes. Tout d'abord, on identifie les observations expérimentales, et de là les phénomènes physiques, à étudier. Ensuite, on développe, dans le cadre de GENERIC, des modèles dont les prédictions sont directement confrontées et comparées à ces mesures expérimentales. Le formalisme GENERIC, qui a été établi pour assurer la compatibilité des solutions avec la thermodynamique, s'applique selon l'algorithme suivant : i) choix des variables d'état ii) détermination de la cinématique réversible ou de Poisson iii) détermination de la cinématique irréversible ou de Riemann iv) spécification de l'énergie totale Φ et du potentiel de dissipation Ψ.

Les systèmes auxquels nous nous sommes intéressés sont les mélanges miscibles : i) binaires constitués d'un fluide simple (e.g. solvant) et d'un polymère et ii) ternaires composés de deux fluides simples (e.g. solvants) et d'un polymère. Chaque composant dans le mélange est décrit par ses propres variables d'état. Le fluide simple est décrit par sa densité de masse ρ_i et par son vecteur densité de la quantité de mouvement linéaire $\mathbf{u}_i$. Le fluide complexe structuré est caractérisé, en plus des deux variables cités ci-dessus, soit par la fonction de distribution de l'espace de configuration ψ ou par son deuxième moment, le tenseur de conformation $\mathbf{m}$. Le mélange formé de n composants ($n = 2$ pour binaire et $n = 3$ pour ternaire) est alors décrit par la densité de la masse totale ρ, le vecteur densité de la quantité de mouvement linéaire $\mathbf{u}$, (n-1) scalaires c_i désignant les fractions

massiques, et (n-1) vecteurs, $\mathbf{w}_i$, représentant les vecteurs densités des quantités de mouvement relatives, et le tenseur d'ordre deux, $\mathbf{m}$, pour caractériser la structure interne.

Les mélanges binaires et ternaires soumis à un écoulement externes sont étudiés respectivement dans le premier et le quatrième articles. Les couplages entre la diffusion, l'écoulement et la déformation de la structure interne apparaissent explicitement dans les équations gouvernant l'évolution temporelle du système étudié. La diffusion dépend anisotropiquement de l'écoulement et de la déformation de la structure interne. Réciproquement, la structure interne est influencée, d'une manière concomitante, par les deux types d'écoulement : externe et interne. Le dernier est produit par la diffusion. Outre cette mutuelle dépendance, des contraintes élastiques sont crées au sein du mélange par les mouvements relatifs (flux de diffusion) et par conséquent modifient le comportement dynamique de l'écoulement. De plus dans les mélanges ternaires, de nouveaux couplages surviennent entre les flux de diffusion dus aux effets d'entraînement qui se génèrent entre les solvants. Dans le processus de la résolution asymptotique des équations d'évolution, nous retrouvons comme cas particuliers les modèles proposées dans la littératures. De plus, les coefficients de transport dépendent explicitement du gradient de la vitesse appliquée, ce qui rend la diffusion fortement anisotrope même en l'absence des contraintes internes.

Afin d'étudier la diffusion viscoélastique dans les mélanges binaires (articles 2 et 3) et ternaires (article 5) en l'absence d'un écoulement externe, nous avons considéré les modèles développés respectivement dans les articles 1 et 4 auxquels nous avons appliqués les contraintes de l'équilibre mécanique et de l'incompressibilité globale. Ces contraintes permettent de simplifier considérablement les équations d'évolution gouvernant l'évolution temporelle du système étudié.

Le deuxième et le troisième articles sont consacrés à l'étude de la diffusion non-Fickienne d'un solvant dans un polymère pour laquelle l'inertie du flux de masse et celle de la conformation sont tenues en considération dans un modèle appelé (c,w,m)-model,. Parmi les modèles obtenus comme cas particuliers de ce modèle, nous avons retrouvé les lois de Fick, les modèles proposés dans la littérature et décrits par les variables d'état : la

concentration c et la contrainte interne σ, et un nouveaux modèle, appelé (c,w)-model. Dans ce dernier modèle, l'influence de la structure interne du polymère est exprimée indirectement par le biais de la dépendance des lois constitutives (coefficient de diffusion, temps de relaxation) de la concentration. À l'aide de ce modèle, nous avons expliqué plusieurs comportements non-Fickiens, notamment le transport Cas II, appelé aussi onde de choc d'Alfrey dû à ses caractéristiques similaires avec les ondes non linéaires. Cette similitude nous a inspirés pour introduire un nouveau concept qui perçoit le transfert de masse comme la propagation d'ondes non linéaires que nous avons alors appelées ondes osmotiques. L'information sur la formation de ces ondes non-linéaires et leur propagation est rendue accessible à l'aide de la méthode des caractéristiques. Dans ce contexte, nous avons introduit un nombre adimensionnel, M_{diff}, appelé nombre de diffusion de Mach, pour réinterpréter et classifier les différents comportements de la diffusion. La diffusion Fickienne, obtenue pour des valeurs de M_{diff} plus petites que l'unité, devient la diffusion subosmotique. Le transport Cas II, obtenu pour des valeurs de M_{diff} plus grandes que l'unité, correspond à la diffusion superosmotique. Nous nous sommes aussi intéressés à la propagation des ondes linéaires pour lesquelles la vitesse de phase et l'atténuation de l'intensité sont calculées analytiquement. Pour une comparaison directe entre les prédictions des modèles (c,w)-model et (c,w,m)-model avec les observations expérimentales prises de la littérature, nous avons résolus numériquement les équations d'évolution, ce qui a nécessité de déterminer l'énergie libre du problème. L'expression de Flory-Huggins est choisie pour la partie du mixage et celles de Maxwell et FENEP pour la partie élastique. Cette dernière a été adéquatement modifiée pour tenir compte d'un éventuel gonflement du polymère suite au processus de la diffusion. Comme le gonflement produit un déplacement des frontières, les équations d'évolution ont été réécrites dans la description matérielle (Lagrangienne) en utilisant la matrice de déformation. L'étude adimensionnelle du modèle (c,w,m)-modèl, met en évidence l'existence de trois paramètres De, de et K qui représentent l'individualité du mélange étudié. Le premier, De, appelé nombre w-Deborah, est exprimé en fonction du nombre de Mach de diffusion M_{diff}. Le second, de, appelé nombre m-Deborah, mesure l'importance

des effets inertiels de la déformation. Le dernier, K, est une constante qui couple la diffusion à la microstructure. Dans la dernière étape, nous avons comparé les prédictions de ces modèles avec des mesures expérimentales prises de la littérature [N. L. Thomas et A. H. Windle, polymer, 19, 255 (1978)] , et un bon accord a été trouvé. Parmi les résultats obtenus, nous arrivons à expliquer le transport Cas II sans supposer la transition vitreuse-caoutchouteuse.

Dans le dernier article, nous avons étendu la description du processus du transfert de masse d'un seul composant à celle de deux composants dans un polymère. Les variables d'état sont : deux scalaires c_1 et c_2 qui représentent les fractions massiques des solvants, deux vecteurs densité des flux de masse $\mathbf{w}_1$ et $\mathbf{w}_2$, et un tenseur du second ordre, $\mathbf{m}$, qui caractérise la structure interne du polymère. Les équations dévolution (8.7)-(8.20), dans lesquelles la diffusion et la déformation de la microstructure sont étroitement couplées, constituent les résultats principaux de cette étude. Dans ces équations, toutes les caractéristiques intrinsèques du mélange solvant-solvant-polymère sont exprimées dans l'énergie libre, la matrice de relaxation des flux Θ et le temps de relaxation λ de la structure interne. La diffusion dans les mélanges ternaires est considérée comme un processus avec un triple inertie : l'inertie provenant des deux flux de masse et celle liée à la structure interne $\mathbf{m}$. Dans cet article, nous avons étudié en détail les deux cas particuliers i) la diffusion sans inertie qui conduit au modèle de Fick généralisé et ii) la diffusion avec une double inertie qui résulte de la réponse retardée des deux flux de masse $\mathbf{w}_1$ et $\mathbf{w}_2$. Dans ce dernier cas, nous avons discuté le phénomène de la propagation des ondes linéaires, et avons calculé leur vitesse de phase et leur atténuation. Dans le domaine des fréquences très larges, cette étude prédit la propagation de deux types d'onde présentant des vitesses constantes. La détection de ces ondes pourrait se révéler un nouvel outil utile pour étudier la diffusion de la matière. Par une analyse adimensionnelle, on observe que le nombre de Deborah devient dans les systèmes ternaires une matrice (2×2), $\mathbf{De}$, qui exprime les effets des couplages entre les flux de masse. Des solutions numériques détaillées sont fournis et comparées avec deux types d'observations expérimentales : i) des mesures obtenues par pervaporation d'un mélange

toluène-benzène par une membrane de polytéréphtalate d'éthyl [F. Suzuki et al. J. Appl. Poly. Sci. 27, 2179 (1982)] et ii) des mesures de sorption dans un polymère vitreux d'un mélanges de deux solvants, l'un exhibant le comportement Fickien et l'autre le comportement Cas II [T. K. Kwei et H. M. Zupko, J. Poly. Sci. Part A2, 7, 867, (1969)].

Comme perspectives qui peuvent découler du travail dévelopé dans cette thèse on peut suggérer que

1. Numériquement :
    - écrire des programmes (codes) pour tester la validité des modèles proposés pour les systèmes en écoulement.
    - raffiner et adapter les programmes déjà écrits pour d'autres problèmes de la diffusion viscoélastiques tel que les gels.
    - tester les modèles développés pour les mélanges ternaires pour d'autres expériences de séparation par pervaporation.
    - développer des méthodes numériques pour les équations proposées semblales à celles développées pour les fluides compressibles.
    - utiliser des méthodes numériques plus précises comme la méthode des éléments finis.
2. Théoriquement :
    - généraliser les modèles proposés au cas de la diffusion non-isotherme dans les mélanges solvant-polymère.
    - généraliser les modèles proposés pour la diffusion isotherme dans les mélanges polymère-polymère.
3. Expérimentalement :
    - détecter les ondes osmotiques.
    - développer des techniques de mesures pour étudier la diffusion par le biais des ondes (voir article 5).
    - étudier la séparation de phase produite par écoulement dans les mélanges ternaires.

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Annexes

```
%=========================================================================
%
%                    modified Maxwell model for CaseII mass transport (Article III, chapitre 6)
%
%=========================================================================
clc, clear,clf,format long,          e=cputime;
N=100;                                    num1=1;        num2=10;       numM=1;
L=1500;
r1=0.1;
tt=r1/N;
%=========================================================================


Avs=0.0;                                  Av=0.0;
Ads=0.0;                                  Ad=0.0;
Ars=0.0;                                  Ar=0.0;
vitesse=1.8*10^(-9);
meq=1.3;  minm=1;

%=========================  data for PMMA  ================================
%vitesse=3.8*10^(-10)m/s a 10C et 1.86*10^(-9)m/s a 24;
Ceq=0.21;       phieq=0.24;
Cm=10^(-8);     Cam=0;          Cm=10^(-3);
qsi=1.15;       % interaction parameter
gammap=1.19;    % polymer material density (g/cm^3)
gammasol=0.79;  % solvent material density  (g/cm^3)
a=phieq/Ceq;
vol=4.05*10^(-5);       %solvent molar volume
RT=8.314*297;
mod=3.3*10^(9);         % elastic modulus (Pa)
viscosity=10^(12);      % viscosity (Pa.s)
lo=0.5*10^(-3);         % film thickness  (m)
CoefDiff=lo*vitesse;    %diffusion coefficient (m^2/s)
pm=mod*vol/(2*RT);
td=(lo^2/CoefDiff);     % diffusion characteristic time scale (s)

S=6.9;                  % diffusion Mach number for the core
s=3.35;                 % diffusion Mach number for the surface

%=========================================================================
%=========================================================================

Dev=(S)^2;      % w-Deborah number for the core
Devs=(s)^2;     % w-Deborah number for the surface

Dem=(viscosity*CoefDiff)/(mod*lo^2);.     % m-Deborah number for the core.
Dems=10.8*(viscosity*CoefDiff)/(mod*lo^2); % m-Deborah number for the surface

%=========================================================================

count=1;
%=========================================================================
```

```
x=zeros(1,N+1);          % coordinate for the thickness of the film
C=Cn*ones(1,N+1);        CC=C;          IC=[C];          CCCC(1)=1; %mass fraction
V=zeros(1,N+1);          VV=V;          IV=[V];          VVV(1)=0;  %front velocity
m=ones(1,N+1);           mm=m;          Im=[m];          mmm(1)=0;  % conformation
J=C.*VV;                 IJ=[ ];        IJN=[ ];                    % solvent mass flux
gradVP=zeros(1,N+1);                    IgradVP=[gradVP];           %polymer velocity gradient
SI=zeros(1,N+1);         ISI=[ ];
Sm=zeros(1,N+1);                        ISm=[Sm];                   %internal stress
viscr=ones(1,N+1);                      % viscosity
Iviscr=[viscr];                         %viscosity
IMach=[ ];
IM=[ ];
Ikm=[ ];
Iks=[ ];
ICs=[ ];IVs=[ ];Ims=[ ]; ISms=[ ];  %    Surface variables

%=========================================================================
for i=1:N+1
x(i)=(i-1)/N;
end
%=============================        INITIAL        Input        ==========
%=========================================================================
%core
F=exp(Ad*(CC-Cn)); % normalized constitutive function for the diffusion coefficient
G=exp(Ar*(CC-Cn)); % normalized constitutive function for the relaxation time inverse
K=Ceq*(CC-Cn)./(1-Ceq*(CC-Cn));
eta=exp(Av*(CC-Cn)); % normalized constitutive function for the viscosity

%surface
Fs=exp(Ads*(CC-Cn));
Gs=exp(Ars*(CC-Cn));
etas=exp(Avs*(CC-Cn));

norma=eta(1)/Dem;
normas=1/Dems;

%=========================
g=(1-a*Ceq*(CC-Cn));
dg=-ones(1,N+1);                        %derivative with respect to phi
ddg=zeros(1,N+1);                       %derivative with respect to phi
%=========================
f=(meq*(1-CC)+CC)/meq;
df=((-meq+1)/(a*Ceq*meq))*ones(1,N+1);
ddf=zeros(1,N+1);
If=[f];
%=========================
Q=g.*f;
dQ=dg.*f+df.*g;
ddQ=ddf.*g+ddg.*f+2*df.*dg;

%=========================

Numera=dQ-dg./mm;
```

```
Denomina=(1-2*qsi*a*Ceq*CC)+a*pm*CC.*(ddQ.*mm-ddg.*log(f.*mm)-g.*(ddf.*df-df.^2)./(f.^2)-
2*dg.*df./f);
R=Numera./Denomina;


%=========================================================================
%=========================  time loop  ===================================
for k=1:L

F=exp(Ad*(CC-Cn));
G=exp(Ar*(CC-Cn));
K=Ceq*(CC-Cn)./(1-Ceq*(CC-Cn));                    KK=Ceq/(1-Ceq);
eta=exp(Av*(CC-Cn));

Fs(1)=exp(Ads*(CC(1)-Cn));                         FFs(1)=exp(Ads*CCCC(1));
Gs(1)=exp(Ars*(CC(1)-Cn));                         GGs(1)=exp(Ars*CCCC(1));
etas(1)=exp(Avs*(CC(1)-Cn));

%=========================== Calculations ================================
%=========================================================================

%=========================  Surface  =====================================

m(1)=mm(1)+r1*K(1)*VV(1)*(mm(1)-mmm(1))/sqrt(mm(1))-r1*K(1)*(VV(1)-VVV(1))*sqrt(mm(1))-
Ceq*r1*VV(1)*sqrt(mm(1))*(CC(1)-CCCC(1))/(1-Ceq*CC(1))^2-(1/Dem)*tt*eta(1)*(f(1)*mm(1)-1);


V(1)=VV(1)-r1*(VV(1)^2-VVV(1)^2)/sqrt(mm(1))-(1/((1-
Ceq*CC(1))^2))*r1*(1/Devs)*FFs(1)*GGs(1)*log(CC(1)/CCCC(1))/sqrt(mm(1))-(1/((1-
Ceq*CC(1))^2))*r1*(1/Devs)*F(1)*G(1)*pm*R(1)*(mm(1)-mmm(1))/sqrt(mm(1))-
tt*Gs(1)*(1/Devs)*VV(1)/((1-Ceq*CC(1))^2);

C(1)=CC(1)-0.5*r1*(VVV(1)+VV(2))*(CC(1)-CCCC(1))/sqrt(mm(1)); %Rankine –Hugoniot relation


gradVP(1)=(N*Ceq/sqrt(mm(1)))*(VV(1)*(CC(1)-CCCC(1))/(1-Ceq*CC(1))^2+CC(1)*(VV(1)-
VVV(1))/(1-Ceq*CC(1)));

meq=m(1);

%=========================================================================
%=========================  Core  ========================================
g=(1-a*Ceq*(CC-Cn));
dg=-ones(1,N+1);
ddg=zeros(1,N+1);
%=========================
f=(meq*(1-CC)+CC)/meq;
df=((-meq+1)/(a*Ceq*meq))*ones(1,N+1);
ddf=zeros(1,N+1);
If=[f];
%=========================
Q=g.*f;
dQ=dg.*f+df.*g;
```

```
ddQ=ddf.*g+ddg.*f+2*df.*dg;

%=========================

Numera=dQ-dg./mm;

Denomina=(1-2*qsi*a*Ceq*CC)+a*pm*CC.*(ddQ.*mm-ddg.*log(f.*mm)-g.*(ddf.*df-df.^2)./(f.^2)-
2*dg.*df./f);
R=Numera./Denomina;

VP=VV.*K;



for i=2:N

m(i)=mm(i)+r1*K(i)*VV(i)*(mm(i)-mm(i-1))/sqrt(mm(i))-r1*K(i)*(VV(i)-VV(i-1))*sqrt(mm(i))-
Ceq*r1*VV(i)*sqrt(mm(i))*(CC(i)-CC(i-1))/(1-Ceq*CC(i))^2-(1/Dem)*tt*eta(i)*(f(i)*mm(i)-1);

%V(i)=VV(i)-r1*(VV(i)^2-VV(i-1)^2)/sqrt(mm(i))-(1/((1-
Ceq*CC(i))^2))*(1/Dev)*r1*F(i)*G(i)*(log(CC(i)/CC(i-1))+pm*R(i)*(mm(i)-mm(i-1)))/sqrt(mm(i))-
tt*(1/Dev)*G(i)*VV(i)/((1-Ceq*CC(i))^2);


V(i)=VV(i)-0.5*r1*(VV(i-1)+VV(i))*(VV(i)-VV(i-1))/sqrt(mm(i))-(1/((1-
Ceq*CC(i))^2))*(1/Dev)*r1*F(i)*G(i)*(log(CC(i)/CC(i-1))+pm*R(i)*(mm(i)-mm(i-1)))/sqrt(mm(i))-
tt*(1/Dev)*G(i)*VV(i)/((1-Ceq*CC(i))^2);

C(i)=CC(i)-0.5*r1*(VV(i-1)+VV(i+1))*(CC(i)-CC(i-1))/sqrt(mm(i)); %Rankine-Hugoniot relation

gradVP(i)=(N*Ceq/sqrt(mm(i)))*(VV(i)*(CC(i)-CC(i-1))/(1-Ceq*CC(i))^2+CC(i)*(VV(i)-VV(i-1))/(1-
Ceq*CC(i)));
end
m(N+1)=mm(N+1)+r1*K(N+1)*VV(N+1)*(mm(N+1)-mm(N))/sqrt(mm(N+1))-r1*K(N+1)*(VV(N+1)-
VV(N))*sqrt(mm(N+1))-Ceq*r1*VV(N+1)*sqrt(mm(N+1))*(CC(N+1)-CC(N+1))/(1-Ceq*CC(N+1))^2-
(1/Dem)*tt*eta(N+1)*(f(N+1)*mm(N+1)-1);

V(N+1)=VV(N+1)-0.5*r1*(VV(N+1)+VV(N))*(VV(N+1)-VV(N))/sqrt(mm(N+1))-(1/((1-
Ceq*CC(N+1))^2))*(1/Dev)*r1*F(N+1)*G(N+1)*(log(CC(N+1)/CC(N+1))+pm*R(N+1)*(mm(N+1)-
mm(N)))/sqrt(mm(N+1))-tt*(1/Dev)*G(N+1)*VV(N+1)/((1-Ceq*CC(N+1))^2);

C(N+1)=CC(N+1)-r1*VV(N)*(CC(N+1)-CC(N))/sqrt(mm(N+1)); %rankine-Hugoniot relation

gradVP(N+1)=(N*Ceq/sqrt(mm(N+1)))*(VV(N+1)*(CC(N+1)-CC(N))/(1-
Ceq*CC(N+1))^2+CC(N+1)*(VV(N+1)-VV(N))/(1-Ceq*CC(N+1)));

%=========================%=========================%=========
%=========================  Swelling  =========================%=========

if( rem(k,numM)==0)
RXX=sqrt(m);
sum1=0.0;
for i=2:2:N
```

```
sum1=sum1+RXX(i);
end
sum2=0.0;
for i=3:2:N-1
sum2=sum2+RXX(i);
end
XX=(1/(3*N))*(RXX(1)+RXX(N+1)+4*sum1+2*sum2);

End

%=========================%=========================%=========
CCCC(1)=1;
if ( abs(XX(1)-1) <=0.2*10^(-3))        mmm(1)=0;  VVV(1)=0;
else                                    mmm(1)=mm(1); VVV(1)=VV(1); end

CC=C;mm=m;VV=V;                         C(1:8),(lo/td)*V(1:8),m(1:8),2*(XX-1)*100,


%=========================        massuptake        =========

Ikm=[Ikm,k];
if( rem(k,numM)==0)
RC=C.*sqrt(m/meq);
M=0.0;
sum1=0.0;
for i=2:2:N
sum1=sum1+RC(i);
end
sum2=0.0;
for i=3:2:N-1
sum2=sum2+RC(i);
end
M=(1/(3*N))*(RC(1)+RC(N+1)+4*sum1+2*sum2);
IM=[IM,M];
IXX=[IXX,XX];
end
%=========================        Store data        =========
for i=1:N+1
if (gradVP(i) > 0 ) gradVP(i)=0;end
if( abs(gradVP(i))<10^(-8)) gradVP(i)=0;end
end

J=C.*V;
SJ=J.*V./(1-Ceq*C);
Sm=(f.*m-1).*g;

for i=1:N+1
if (Sm(i) < 10^(-12)) Sm(i)=0 ;end
end

Mach=V./sqrt(abs(F.*G.*(1+pm*m.*C.*R./(1-Ceq*C))./(Dev*(1-Ceq*C).^2)));
if( rem(k,10)==0)
IJN=[IJN,J(N+1)];
```

```
end

if( rem(k,1)==0 & k<80)

ICs=[ICs,C(1)];
IVs=[IVs,V(1)];
Ims=[Ims,m(1)];
ISms=[ISms,Sm(1)];
IgradVPs=[IgradVPs,gradVP(1)];
end

if(k<=30 & rem(k,num1)==0)
count=count+1;
Iks=[Iks,count];

%=========================================================================
if (abs(gradVP(1)) ~= 0 )viscr(1)=normas*eta(1)*abs(Sm(1)/(gradVP(1)));end
for i=2:N+1
if (abs(gradVP(i)) ~= 0 ) viscr(i)=norma*eta(i)*abs(Sm(i)/(gradVP(i)));
%if(minm >= viscr(i)) minm=viscr(i);end
end
if (C(i)<=10^(-6) )                viscr(i)=1;end
%if (C(i)>=0.99)                   viscr(i)=minm;   end
%=========================================================================
end
%IMach=[IMach;Mach];
IJ=[IJ;J];
IC=[IC;C];
IV=[IV;V];
ISJ=[ISJ;SJ];
Im=[Im;m];
ISm=[ISm;Sm];
IgradVP=[IgradVP;gradVP];
Iviscr=[Iviscr;viscr];
end
if( k>20 & rem(k,num2)==0)
count=count+1;
Iks=[Iks,count];
%=========================================================================
if (abs(gradVP(1)) ~= 0 )viscr(1)=normas*eta(1)*abs(Sm(1)/(gradVP(1)));end
for i=2:N+1
if (abs(gradVP(i)) ~= 0 ) viscr(i)=norma*eta(i)*abs(Sm(i)/(gradVP(i)));
%if(minm > viscr(i)) minm=viscr(i);end
end
if (C(i)<=10^(-6) )                viscr(i)=1;end
%if (C(i)>=0.99)                   viscr(i)=minm;   end
end
%=========================================================================
%IMach=[IMach;Mach];
IC=[IC;C];
IV=[IV;V];
IJ=[IJ;J];
ISJ=[ISJ;SJ];
```

```
Im=[Im;m];
ISm=[ISm;Sm];
IgradVP=[IgradVP;gradVP];
Iviscr=[Iviscr;viscr];
end

ksmax=max(Iks);
%=============================================================================
end
vis=ones(1,ksmax);
Tvis=[];
for i=1:ksmax
if (abs(IgradVP(i,1)) ~= 0   )        vis(i)=normas*abs(ISm(i,1)/(IgradVP(i,1)));end
end
Tvis=[Tvis;vis];
for j=2:N+1
for i=1:ksmax
if (abs(IgradVP(i,j)) ~= 0   )        vis(i)=norma*abs(ISm(i,j)/(IgradVP(i,j)));
%if(minm >= vis(i)) minm=vis(i);end
end
if (IC(i,j)<=10^(-7)  )               vis(i)=1;end
%if (IC(i,j)>=0.9  )                          vis(i)=minm;      end
end
Tvis=[Tvis;vis];
end
ttr=(tt*td/3600)*Ikm;
r=ones(size(ttr));
r=sqrt(ttr);
e=(cputime-e);
loglog(IC',Tvis);pause
loglog(abs(IgradVP'), Tvis);pause

%=============================================  Plot data  ==========================
plot(ttr,IM),title('real mass uptake');grid,xlabel('time(hr)'), ylabel('IM'),pause
plot(ttr(1:79),ICs,'*'),title('IC(1) surface'),grid,pause;
plot(ttr(1:79),(lo/td)*IVs,'*'),title('IV(1) surface'),grid,pause;
plot(ttr(1:79),Ims,'*'),title('Im surface'),grid,pause;
plot(ttr(1:79),mod*ISms,'*'),title('surface Stress profiles'),grid,pause;
plot(ttr(1:79),IgradVPs,'*'),title('IgradVP(1)'),grid,pause;

%=============================================================================
plot(IC(:,2)','*'),title('IC(2) surface'),grid,pause;
plot((lo/td)*IV(:,2)','*'),title('IV(2) surface'),grid,pause;
plot(Im(:,2)','*'),title('Im(2) surface'),grid,pause;
plot(mod*ISm(:,2)','*'),title('surface Stress profiles(2)'),grid, xlabel('normalized time'),pause;
plot(IgradVP(:,2)','*'),title('IgradVP(2)'),grid,pause;
%=============================================================================
plot(x,IC'),title('Concentration profiles'),grid, xlabel('normalized lenght'), ylabel('C/Ceq');pause
plot(x,(lo/td)*IV'),title('Velocityprofiles'),grid,xlabel('normalized lenght'),ylabel('Velocity');pause
%plot(x,IMach'),title('Mach number'), xlabel('normalized lenght'), ylabel('Mach');pause

plot(x,IJ'),title('IJ'); pause;
plot(IJN,'o'),title('flux a la sortie'),grid,xlabel('normalized time'), ylabel('output flux');pause
```

```
plot(IJ(:,N/2),'o'),title('flux au milieu'),grid,xlabel('normalized time'), ylabel('half width flux'),pause
plot(x,ISJ'),title('JJ stress profiles'),grid, xlabel('normalized lenght'), ylabel('SJ');pause

plot(x,Im'),title('Conformation profiles'), grid,xlabel('normalized lenght'), ylabel('m/meq');pause
plot(x,mod*ISm'),title('internalStressprofiles'),grid,xlabel('normalizedlenght'),ylabel('Stress');pause;
%=============================================================
plot(x,IgradVP),title('gradVP versus x'),grid;pause

loglog(abs(IgradVP(1:3:ksmax,:)),Iviscr(1:3:ksmax,:));title('loglogplot(IgradVP(1:3:ksmax,:),Iviscr)');paus
e
loglog(abs(IgradVP(ksmax/4,:)),Iviscr(ksmax/4,:));title('loglogplot(IgradVP(ksmax/4,:),Iviscr)');pause
loglog(abs(IgradVP(ksmax/2,:)),Iviscr(ksmax/2,:));title('loglogplot(IgradVP(ksmax/2,:),Iviscr)');pause
loglog(abs(IgradVP(3*ksmax/4,:)),Iviscr(3*ksmax/4,:));title('loglogplot(IgradVP(3*ksmax/4,:),Iviscr)');pau
se
loglog(abs(IgradVP(ksmax,:)),Iviscr(ksmax,:));title('loglogplot(IgradVP(ksmax,:),Iviscr)');pause
%=============================================================

%=============================================================


%=============================================================
loglog(abs(IC(1:3:ksmax,:)),Iviscr(1:3:ksmax,:));title('loglogplot(IC(1:3:ksmax,:),Iviscr)');pause
loglog(abs(IC(ksmax:-5:1,:)),Iviscr(ksmax:-5:1,:));title('loglogplot(IC(ksmax:-5:1,:),Iviscr)');pause
loglog(abs(IC(ksmax/4,:)),Iviscr(ksmax/4,:));title('loglogplot(IC(ksmax/4,:),Iviscr)');pause
loglog(abs(IC(ksmax/2,:)),Iviscr(ksmax/2,:));title('loglogplot(IC(ksmax/2,:),Iviscr)');pause
loglog(abs(IC(3*ksmax/4,:)),Iviscr(3*ksmax/4,:));title('loglogplot(IC(3*ksmax/4,:),Iviscr)');pause
loglog(abs(IC(ksmax,:)),Iviscr(ksmax,:));title('loglogplot(IC(ksmax,:),Iviscr)');pause
%=============================================================

plot(r,IM),title('mass uptake versus sqrt(time)'),grid,xlabel('sqrt(normalized time)'),ylabel('M/Meq');pause
plot(ttr,IM),title('real mass uptake');grid,xlabel('time(hr)'), ylabel('IM'),pause
plot(log(ttr(2:L/numM)),log(IM(2:L/numM)));grid,title('log-log plot of real mass uptake');pause
load datvi;
plot(time,VI,'*',ttr,2*(IXX-1)*100);title('volume increase'); pause;
load datatom;
plot(temps,mass,'*',ttr,IM);title('polymer weight gain'); pause;
%=============================================================


%save dacvm22 IM IC IV IJN IJ ISJ Im ISm Ikm Iks IMach x IXX ttr r ICs IVs Ims ISms Iviscr IgradVP
Tvis ksmax Dem Dems Dev Devs N L r1 tt pm mod lo td vol S s qsi Ceq a phieq Cn Ad Ads Av Avs Ar
Ars;
```

```
%=========================================================================
%
%                    mofdified FENEP model for Case II mass transport (article III, chapitre 6)
%
%=========================================================================

%=========================================================================
clc, clear,clf,format long,          e=cputime;
N=100;                                    num1=1;          num2=100;        numM=1;
L=3000;
r1=0.05;
tt=r1/N;
%=========================================

Avs=0.0;                                  Av=0.0;
Ads=0.0;                                  Ad=0.0;
Ars=0.0;                             Ar=0.0;
vitesse=1.8*10^(-9);
meq=1;minm=1;
Ro=2;                                Ro2=Ro^2;        z=Ro2/(1+Ro2);
%=========================           data for PMMA  ==========================
%vitesse=3.8*10^(-10)m/s a 10C et 1.86*10^(-9)m/s a 24;
Ceq=0.21;        phieq=0.24;
Cn=10^(-8);      Cam=0;          Cm=10^(-3);
qsi=1.15;        % interaction parameter
gammap=1.19;     % polymer material density (g/cm^3)
gammasol=0.79;   % solvent material density (g/cm^3)
a=phieq/Ceq;
vol=4.05*10^(-5);          %solvent molar volume
RT=8.314*297;
mod=3.3*10^(9);            % elastic modulus (Pa)
viscosity=10^(12);         % viscosity        (Pa.s)
lo=0.5*10^(-3);            %film thickness  (m)
CoefDiff=lo*vitesse;       %diffusion coefficient (m^2/s)
pm=mod*vol/(2*RT);
td=(lo^2/CoefDiff);        % diffusion characteristic time scale (s)

S=6.9;                     % diffusion Mach number for the core
s=3.35;                    % diffusion Mach number for the surface
%=========================================================================
%=========================================================================
Dev=(S)^2;
Devs=(s)^2;

Dem=(viscosity*CoefDiff)/(mod*lo^2);
Dems=10.8*Dem;

norma=1/Dem;normas=1/Dems;
%=========================================================================
%=========================================================================

count=1;
```

```
%=========================================================
x=zeros(1,N+1);
C=Cn*ones(1,N+1);      CC=C;          IC=[C];          CCCC(1)=1;
V=zeros(1,N+1);        VV=V;          IV=[V];          VVV(1)=0;
m=ones(1,N+1);         mm=m;          Im=[m];          mmm(1)=0;
J=C.*VV;               IJ=[];         IJN=[];
gradVP=zeros(1,N+1);                  IgradVP=[gradVP];
SJ=zeros(1,N+1);              ISJ=[];
Sm=zeros(1,N+1);                      ISm=[Sm];
viscr=ones(1,N+1);                    Iviscr=[viscr];
IMach=[];
IM=[];
Ikm=[];
Iks=[];
ICs=[];IVs=[];Ims=[];ISms=[];

%=========================================================
for i=1:N+1
x(i)=(i-1)/N;
end
%=============================      INITIAL      Input      ==========
%=========================================================
F=exp(Ad*(CC-Cn));
G=exp(Ar*(CC-Cn));
K=Ceq*(CC-Cn)./(1-Ceq*(CC-Cn));
eta=exp(Av*(CC-Cn));

Fs=exp(Ads*(CC-Cn));
Gs=exp(Ars*(CC-Cn));

etas=exp(Avs*(CC-Cn));


%=========================
g=(1-a*Ceq*(CC-Cn));
dg=-ones(1,N+1);          %derivative with respect to phi
ddg=zeros(1,N+1);         %derivative with respect to phi
%=========================
f=(1-CC)+CC/(meq);
df=((-1+1/meq)/(a*Ceq))*ones(1,N+1);
ddf=zeros(1,N+1);
If=[f];
%=========================
T=-Ro2*log(1-z*f.*mm/Ro2);
dT=Ro2*z*df.*mm./(Ro2-z*f.*mm);
ddT=Ro2*z*mm.*(ddf.*(Ro2-z*f.*mm)+z*mm.*df.^2)/((Ro2-z*f.*mm).^2);

Q=g.*T;
dQ=dg.*T+g.*dT;
ddQ=ddT.*g+ddg.*T+2*dT.*dg;

%=========================
Numera=(Ro2*z./(Ro2-z*f.*mm)).*(f.*dg+Ro2*df.*g./(Ro2-z*f.*mm))-dg./mm;
```

```
Denomina=(1-2*qsi*a*Ceq*CC)+a*pm*CC.*(ddQ-ddg.*log(z*f.*mm)-g.*(ddf.*f-df.^2)./(f.^2)-
2*dg.*df./f);

R=Numera./Denomina;

%=============================          time loop          ============================
for k=1:L

F=exp(Ad*(CC-Cn));
G=exp(Ar*(CC-Cn));
K=Ceq*(CC-Cn)./(1-Ceq*(CC-Cn));
eta=exp(Av*(CC-Cn));

Fs(1)=exp(Ads*(CC(1)-Cn));                    FFs(1)=exp(Ads*CCCC(1));
Gs(1)=exp(Ars*(CC(1)-Cn));                    GGs(1)=exp(Ars*CCCC(1));
etas(1)=exp(Avs*(CC(1)-Cn));

%============================== Calculations ==============================
%==========================================================================

%=============================          Surface ============================

m(1)=mm(1)+r1*K(1)*(VV(1)/sqrt(mm(1)))*(mm(1)-mmm(1))-r1*K(1)*(VV(1)-VVV(1))*sqrt(mm(1))-
Ceq*r1*VV(1)*sqrt(mm(1))*(CC(1)-CCCC(1))/(1-Ceq*CC(1))^2-
(1/Dems)*tt*etas(1)*(z*Ro2*f(1)*mm(1)/(Ro2-z*f(1)*mm(1))-1)/z;

V(1)=VV(1) )-0.5*r1*(VVV(1)+VV(1))*(VV(1)-VVV(1))/sqrt(mm(1))-(1/((1-
Ceq*CC(1))^2))*r1*(1/Devs)*FFs(1)*GGs(1)*log(CC(1)/CCCC(1))/sqrt(mm(1))-(1/((1-
Ceq*CC(1))^2))*r1*(1/Devs)*F(1)*G(1)*pm*R(1)*(mm(1)-mmm(1))/sqrt(mm(1))-
tt*Gs(1)*(1/Devs)*VV(1)/((1-Ceq*CC(1))^2 ;

C(1)=CC(1)-0.5*r1*(VVV(1)+VV(2))*(CC(1)-CCCC(1))/sqrt(mm(1)); % Rankine-Hugoniot relation

gradVP(1)=(N*Ceq/sqrt(mm(1)))*(VV(1)*(CC(1)-CCCC(1))/(1-Ceq*CC(1))^2+CC(1)*(VV(1)-
VVV(1))/(1-Ceq*CC(1)));

meq=m(1);

%==========================================================================
%=============================          Core          ============================
g=(1-a*Ceq*(CC-Cn));
dg=-ones(1,N+1);
ddg=zeros(1,N+1);
%=============================
f=(meq*(1-CC)+CC)/meq;
df=((-meq+1)/(a*Ceq*meq))*ones(1,N+1);
ddf=zeros(1,N+1);
If=[f];
%=============================
T=-Ro2*log(1-z*f.*mm/Ro2);
dT=Ro2*z*df.*mm./(Ro2-z*f.*mm);
ddT=Ro2*z*mm.*(ddf.*(Ro2-z*f.*mm)+z*mm.*df.^2)/((Ro2-z*f.*mm).^2);
```

```
Q=g.*T;
dQ=dg.*T+g.*dT;
ddQ=ddT.*g+ddg.*T+2*dT.*dg;

%=================================
Numera=(Ro2*z./(Ro2-z*f.*mm)).*(f.*dg+Ro2*df.*g./(Ro2-z*f.*mm))-dg./mm;
Denomina=(1-2*qsi*a*Ceq*CC)+a*pm*CC.*(ddQ-ddg.*log(z*f.*mm)-g.*(ddf.*f-df.^2)./(f.^2)-
2*dg.*df./f);
R=Numera./Denomina;
VP=VV.*K;

for i=2:N

m(i)=mm(i)+r1*K(i)*VV(i)*(mm(i)-mm(i-1))/sqrt(mm(i))-r1*K(i)*sqrt(mm(i))*(VV(i)-VV(i-1))-
Ceq*r1*VV(i)*sqrt(mm(i))*(CC(i)-CC(i-1))/(1-Ceq*CC(i))^2-
(1/Dem)*tt*eta(i)*(Ro2*z*f(i)*mm(i)/(Ro2-z*f(i)*mm(i))-1)/z;

V(i)=VV(i)-0.5*r1*(VV(i-1)+VV(i))*(VV(i)-VV(i-1))/sqrt(mm(i))-(1/((1-
Ceq*CC(i))^2))*(1/Dev)*r1*F(i)*G(i)*(log(CC(i)/CC(i-1))+pm*R(i)*(mm(i)-mm(i-1)))/sqrt(mm(i))-
tt*(1/Dev)*G(i)*VV(i)/((1-Ceq*CC(i))^2);

C(i)=CC(i)-0.5*r1*(VV(i-1)+VV(i+1))*(CC(i)-CC(i-1))/sqrt(mm(i));% Rankine-Hugoniot relation

gradVP(i)=(N*Ceq/sqrt(mm(i)))*(VV(i)*(CC(i)-CC(i-1))/(1-Ceq*CC(i))^2+CC(i)*(VV(i)-VV(i-1))/(1-
Ceq*CC(i)));


end
m(N+1)=mm(N+1)+r1*K(N+1)*VV(N+1)*(mm(N+1)-mm(N))/sqrt(mm(N+1))-r1*K(N+1)*(VV(N+1)-
VV(N))*sqrt(mm(N+1))-Ceq*r1*VV(N+1)*sqrt(mm(N+1))*(CC(N+1)-CC(N+1))/(1-Ceq*CC(N+1))^2-
(1/Dem)*tt*eta(N+1)*(Ro2*z*f(N+1)*mm(N+1)/(Ro2-z*f(N+1)*mm(N+1))-1)/z;

V(N+1)=VV(N+1)-0.5*r1*(VV(N+1)+VV(N))*(VV(N+1)-VV(N))/sqrt(mm(N+1))-(1/((1-
Ceq*CC(N+1))^2))*(1/Dev)*r1*F(N+1)*G(N+1)*(log(CC(N+1)/CC(N+1))+pm*R(N+1)*(mm(N+1)-
mm(N)))/sqrt(mm(N+1))-tt*(1/Dev)*G(N+1)*VV(N+1)/((1-Ceq*CC(N+1))^2);

C(N+1)=CC(N+1)-r1*VV(N)*(CC(N+1)-CC(N))/sqrt(mm(N+1));% Rankine-Hugoniot relation

gradVP(N+1)=(N*Ceq/sqrt(mm(N+1)))*(VV(N+1)*(CC(N+1)-CC(N))/(1-
Ceq*CC(N+1))^2+CC(N+1)*(VV(N+1)-VV(N))/(1-Ceq*CC(N+1)));

%=================================%=================================%=================
%=================================%=================================%=================
if( rem(k,numM)==0)
RXX=sqrt(m);

sum1=0.0;
for i=2:2:N
sum1=sum1+RXX(i);
end
sum2=0.0;
for i=3:2:N-1
sum2=sum2+RXX(i);
```

```
end
XX=(1/(3*N))*(RXX(1)+RXX(N+1)+4*sum1+2*sum2);
End
%=============================================================================
CCCC(1)=1;
if ( (XX(1)-1) <=0.2*10^(-3))                    mmm(1)=0;  VVV(1)=0;
else                                          mmm(1)=mm(1); VVV(1)=VV(1); end


CC=C;mm=m;VV=V;                               C(1:8),(lo/td)*V(1:8),m(1:8),2*(XX-1)*100,

%=========================                    massuptake                    ========================

Ikm=[Ikm,k];
if( rem(k,numM)==0)
RC=C.*sqrt(m/meq);
M=0.0;
sum1=0.0;
for i=2:2:N
sum1=sum1+RC(i);
end
sum2=0.0;
for i=3:2:N-1
sum2=sum2+RC(i);
end
M=(1/(3*N))*(RC(1)+RC(N+1)+4*sum1+2*sum2);
IM=[IM,M];
IXX=[IXX,XX];
end

%=============================                Store data                    ==================
for i=1:N+1
if (gradVP(i) > 0 ) gradVP(i)=0;end
if( abs(gradVP(i))<10^(-8)) gradVP(i)=0;end
end
Mach=V./sqrt(abs(F.*G.*(1+pm*m.*C.*R./(1-Ceq*C))./(Dev*(1-Ceq*C).^2)));
J=C.*V;
SJ=J.*V./(1-Ceq*C);
Sm=(Ro2*z*f.*m./(Ro2-z*f.*m)-1).*g;

for i=1:N+1
if (Sm(i) ==0) Sm(i)=0;end
if (Sm(i) < 10^(-12)) Sm(i)=0;end
end

if( rem(k,10)==0)
IJN=[IJN,J(N+1)];
end

if( rem(k,1)==0 & k<180)

ICs=[ICs,C(1)];
IVs=[IVs,V(1)];
```

```
Ims=[Ims,m(1)];
ISms=[ISms,Sm(1)];
IgradVPs=[IgradVPs,gradVP(1)];
end

if(k<=20 & rem(k,num1)==0)
count=count+1;
Iks=[Iks,count];

%=============================================================================
%=============================================================================
if (abs(gradVP(1)) ~= 0 )viscr(1)=normas*eta(1)*abs(Sm(1)/(gradVP(1)));end
if (C(1)<=10^(-6) )                viscr(1)=1;end

for i=2:N+1
if (abs(gradVP(i)) ~= 0 ) viscr(i)=norma*eta(i)*abs(Sm(i)/(gradVP(i)));end
if (C(i)<=10^(-6) )                viscr(i)=1;end
end

%=============================================================================
%=============================================================================
IMach=[IMach;Mach];
IJ=[IJ;J];
IC=[IC;C];
IV=[IV;V];
ISJ=[ISJ;SJ];
Im=[Im;m];
ISm=[ISm;Sm];
IgradVP=[IgradVP;gradVP];
Iviscr=[Iviscr;viscr];
end


if( k>20 & rem(k,num2)==0)
count=count+1;
Iks=[Iks,count];
%=============================================================================
%=============================================================================
if (abs(gradVP(1)) ~= 0 )viscr(1)=normas*eta(1)*abs(Sm(1)/(gradVP(1)));end
if (C(1)<=10^(-6) )                viscr(1)=1;end

for i=2:N+1
if (abs(gradVP(i)) ~= 0 ) viscr(i)=norma*eta(i)*abs(Sm(i)/(gradVP(i))); end
if (C(i)<=10^(-6) )                viscr(i)=1;end
end
%=============================================================================
%=============================================================================
IMach=[IMach;Mach];
IC=[IC;C];
IV=[IV;V];
IJ=[IJ;J];
ISJ=[ISJ;SJ];
Im=[Im;m];
```

```
lSm=[lSm;Sm];
lgradVP=[lgradVP;gradVP];
lviscr=[lviscr;viscr];
end


ksmax=max(lks);
end
%=============================================================================

vis=ones(1,ksmax);
Tvis=[];


for i=1:ksmax
if (abs(lgradVP(i,1)) ~= 0   )      vis(i)=normas*abs(lSm(i,1)/(lgradVP(i,1)));end
if (lC(i,1)<=10^(-6)  )             vis(i)=1;end
end
Tvis=[Tvis;vis];
for j=2:N+1
for i=1:ksmax
if (abs(lgradVP(i,j)) ~= 0   )      vis(i)=norma*abs(lSm(i,j)/(lgradVP(i,j))); end
if (lC(i,j)<=10^(-6)  )             vis(i)=1;end

end
Tvis=[Tvis;vis];
end


ttr=(tt*td/3600)*lkm;
r=ones(size(ttr));
r=sqrt(ttr);
e=(cputime-e);
loglog(lC',Tvis);pause
loglog(abs(lgradVP'), Tvis);pause

%=============================================  Plot data  ============================================
plot(ttr(1:179),lCs,'*'),title('lC(1) surface'),grid,pause;
plot((lo/td)*lVs,'*'),title('lV(1) surface'),grid,pause;
plot(lms,'*'),title('lm surface'),grid,pause;
plot(mod*lSms,'*'),title('surface Stress profiles'),grid,pause;
plot(lgradVPs,'*'),title('lgradVP(1)'),grid,pause;

%=============================================================================
plot(lC(:,2)','*'),title('lC(2) surface'),grid,pause;
plot((lo/td)*lV(:,2)','*'),title('lV(2) surface'),grid,pause;
plot(lm(:,2)','*'),title('lm(2) surface'),grid,pause;
plot(mod*lSm(:,2)','*'),title('surface Stress profiles(2)'),grid, xlabel('normalized time'),pause;
plot(lgradVP(:,2)','*'),title('lgradVP(2)'),grid,pause;
%=============================================================================
plot(x,lC'),title('Concentration profiles'),grid, xlabel('normalized lenght'), ylabel('C/Ceq');pause
plot(x,(lo/td)*lV'),title('Velocityprofiles'),grid,xlabel('normalized lenght'),ylabel('Velocity');pause
plot(x,lMach'),title('Mach number'), xlabel('normalized lenght'), ylabel('Mach');pause
```

```
plot(x,IJ'),title('IJ'); pause;
plot(IJN,'o'),title('flux a la sortie'),grid,xlabel('normalized time'), ylabel('output flux');pause
plot(IJ(:,N/2),'o'),title('flux au milieu'),grid,xlabel('normalized time'), ylabel('half width flux'),pause
plot(x,ISJ'),title('JJ stress profiles'),grid, xlabel('normalized lenght'), ylabel('SJ');pause

plot(x,Im'),title('Conformation profiles'), grid,xlabel('normalized lenght'), ylabel('m/meq');pause
plot(x,mod*ISm'),title('internalStressprofiles'),grid,xlabel('normalizedlenght'),ylabel('Stress');pause;
%=========================================================

plot(x,IgradVP),title('gradVP versus x'),grid;pause

loglog(abs(IgradVP(1:3:ksmax,:)),Iviscr(1:3:ksmax,:));title('loglogplot(IgradVP(1:3:ksmax,:),Iviscr)');paus
e
loglog(abs(IgradVP(ksmax/4,:)),Iviscr(ksmax/4,:));title('loglogplot(IgradVP(ksmax/4,:),Iviscr)');pause
loglog(abs(IgradVP(ksmax/2,:)),Iviscr(ksmax/2,:));title('loglogplot(IgradVP(ksmax/2,:),Iviscr)');pause
loglog(abs(IgradVP(3*ksmax/4,:)),Iviscr(3*ksmax/4,:));title('loglogplot(IgradVP(3*ksmax/4,:),Iviscr)');pau
se
loglog(abs(IgradVP(ksmax,:)),Iviscr(ksmax,:));title('loglogplot(IgradVP(ksmax,:),Iviscr)');pause
%=========================================================



%=========================================================
loglog(abs(IC(1:3:ksmax,:)),Iviscr(1:3:ksmax,:));title('loglogplot(IC(1:3:ksmax,:),Iviscr)');pause
loglog(abs(IC(ksmax:-5:1,:)),Iviscr(ksmax:-5:1,:));title('loglogplot(IC(ksmax:-5:1,:),Iviscr)');pause
loglog(abs(IC(ksmax/4,:)),Iviscr(ksmax/4,:));title('loglogplot(IC(ksmax/4,:),Iviscr)');pause
loglog(abs(IC(ksmax/2,:)),Iviscr(ksmax/2,:));title('loglogplot(IC(ksmax/2,:),Iviscr)');pause
loglog(abs(IC(3*ksmax/4,:)),Iviscr(3*ksmax/4,:));title('loglogplot(IC(3*ksmax/4,:),Iviscr)');pause
loglog(abs(IC(ksmax,:)),Iviscr(ksmax,:));title('loglogplot(IC(ksmax,:),Iviscr)');pause
%=========================================================

plot(r,IM),title('mass uptake versus sqrt(time)'),grid,xlabel('sqrt(normalized time)'),ylabel('M/Meq');pause
plot(ttr,IM),title('real mass uptake');grid,xlabel('time(hr)'), ylabel('IM'),pause
plot(log(ttr(2:L/numM)),log(IM(2:L/numM)));grid,title('log-log plot of real mass uptake');pause

plot(ttr,2*(IXX-1)*100);title('volume increase'); pause
load datvi;
plot(time,VI,'*',ttr,2*(IXX-1)*100);title('volume increase'); pause;
load datatom;
plot(temps,mass,'*',ttr,IM);title('polymer weight gain'); pause;
%=========================================================


%save datf6 IM IC IV IJN IJ ISJ Im ISm Ikm Iks IMach x IXX ttr r ICs IVs Ims ISms Iviscr IgradVP Tvis
ksmax Dem Dems Dev Devs N L r1 tt pm Ro mod lo td vol S s qsi Ceq a Ad Ads Av Avs Ar Ars;

%save df2 IM IC IV IJN IJ ISJ Im ISm Ikm Iks IMach x IXX ttr r ICs IVs Ims ISms Iviscr IgradVP Tvis
ksmax Dem Dems Dev Devs N L r1 tt pm Ro mod lo td vol S s qsi Ceq Ad Ads Av Avs Ar Ars;
```

```
%=========================================================================
%
%                          modified        (c1,c2) model (article 5, Chapitre 8)
%=========================================================================

clc, clear,clf,format long,          e=cputime;
N=15;                                     num1=50;       num2=50;       numM=1;
L=4000;
r1=0.05;

tt=r1/(N*N);

%=========================  data for benzene2 - toluene1  /PET ==================
        zt=140; zb=290; % material constant
        fi0=0;                  % toluene
        lo=3.5*10^(-6) ;        %membrane thickness

        %fi=ai*Ci;       rhoi*fi=Cdi=rho*Ci; rhoi== gammai;

% mass densities
rho1=0.47;
rho2=0.4715;
rho=0.7337;

%fip=1-0.0123-0.0117;
% interaction parameters
qsi12=0;
qsi2p=5.52;
qsi1p=5.57;
% mass
Cd2=5.64*10^(-3);
Cd1=Cd2;
Ceq2=Cd2/rho;
Ceq1=Cd1/rho;
fip=1-Cd1/rho1-Cd2/rho2;
Cdp=rho-Cd1-Cd2;
rhop=Cdp/fip;
a1=rho/rho1;
a2=rho/rho2;
ap=rho/rhop;
ex=exp(zt*Cd1+zb*Cd2);
M1=92;
M2=78;
%self diffusion coefficients
D10=1.18*M1*1.2*10^(-14)/rho;
D20=1.18*M2*1.4*10^(-14)/rho;
%diffusion charcateristic time scales
td11=(lo^2/D10);
td22=(lo^2/D20); b1=td11/td22;
% molar volumes
VVV2=0.894*10^(-4);
```

```
VVV1=1.068*10^(-4);
p=VVV1/VVV2;

%=========================================================
count=1;count1=1;
%=========================================================

Cn=10^(-5);
C1=Cn*ones(1,N+1);      CC1=C1;                 IC1=[];
C2=Cn*ones(1,N+1);      CC2=C2;                 IC2=[];

CC1(1)=1; C1(1)=1;                      CC1(N+1)=0; C1(N+1)=0;
CC2(1)=Ceq2/Ceq1; C2(1)=Ceq2/Ceq1;      CC2(N+1)=0; C2(N+1)=0;

W1=0;W2=0;

D11=ones(1,N+1);        D12=zeros(1,N+1); D21=zeros(1,N+1);     D22=ones(1,N+1);

IWN1=[];
IWN2=[];
IM=[];
Ikm=[];
%=========================================================
%=========================================================
for i=1:N+1
x(i)=(i-1)/N;
end

%=============================        time loop        ==============================

for k=1:L

%H=1-Ceq1*CC1-CC2*Ceq2;
H=ones(1,N+1);

for i=2:N

C1(i)=CC1(i)+r1*H(i)*(D11(i+1)*CC1(i+1)-(D11(i+1)+D11(i))*CC1(i)+D11(i)*CC1(i-
1))+xx*r1*H(i)*(D12(i+1)*CC2(i+1)-(D12(i+1)+D12(i))*CC2(i)+D12(i)*CC2(i-1));

C2(i)=CC2(i)+r1*H(i)*b1*(D21(i+1)*CC1(i+1)-(D21(i+1)+D21(i))*CC1(i)+D21(i)*CC1(i-
1))+r1*H(i)*b1*(D22(i+1)*CC2(i+1)-(D22(i+1)+D22(i))*CC2(i)+D22(i)*CC2(i-1));


end

W1=-N*(D11(N+1)*(C1(N+1)-C1(N))+D12(N+1)*(C2(N+1)-C2(N)));
W2=-b1*N*(D21(N+1)*(C1(N+1)-C1(N))+D22(N+1)*(C2(N+1)-C2(N)));

%=============================  Calcul des Dij  ==============================


Cp=1-xx*Ceq1*C1-Ceq1*C2;      fi1=xx*a1*Ceq1*C1;      fi2=a2*Ceq1*C2;
```

```
D11=(1./(Cp)).*(a1*(1-Ceq1*C1).*(1-2*fi1*qsi1p)-(M2/M1)*(D20/D10)*(qsi12-qsi1p-
qsi2p*p)*fi1.*fi2).*exp(rho*Ceq1*(zt*C1+zb*C2));

D12=(1./(Cp)).*((qsi12-qsi1p-qsi2p*p)*a2*fi1.*(1-Ceq1*C1)-(M2/M1)*(D20/D10)*p*(1-
2*qsi1p*fi2).*fi1).*exp(rho*Ceq1*(zt*C1+zb*C2));

D21=(1./(Cp)).*((a1*(1-Ceq1*C2).*fi2-(M1/M2)*(D10/D20)*fi1.*fi2)*(qsi12-qsi1p-
qsi2p*p)).*exp(rho*Ceq1*(zt*C1+zb*C2));


D22=(1./(Cp)).*(p*a2*(1-Ceq1*C2).*(1-2*qsi2p*fi2)-(M1/M2)*(D10/D20)*fi1.*fi2.*(qsi12-qsi1p-
qsi2p*p)).*exp(rho*Ceq1*(zt*C1+zb*C2));

%=========================%=========================%=========

CC1=C1;                          C1(1:15),Ceq1*C2(1:15)/Ceq2,
CC2=C2;

%=========================          massuptake          =========

if( rem(k,numM)==0)
C=Ceq1*(C1+C2)/(Ceq1+Ceq2);

RC=(1-Ceq1-Ceq2)*C./(1-Ceq1*C);
M=0.0;
sum1=0.0;
for i=2:2:N
sum1=sum1+RC(i);
end
sum2=0.0;
for i=3:2:N-1
sum2=sum2+RC(i);
end
M=(1/(3*N))*(RC(1)+RC(N+1)+4*sum1+2*sum2);
IM=[IM,M];
Ikm=[Ikm,k];
end
%=========================          Store data          =========

if( round(k*tt*td11)<0.1001 & round(k*tt*td11)>0.09999 & round(k*tt*td11)==0.1)
C10=C1;C20=C2;

end
if(k<=200 & rem(k,num1)==0)
count=count+1;
IWN1=[IWN1,W1];
IWN2=[IWN2,W2];
IC1=[IC1;C1];

IC2=[IC2;C2];
```

```
lkf=[lkf,k];
lks=[lks,count];
end
if( k>200 & rem(k,num2)==0)
count=count+1;
lks=[lks,count];
IWN1=[IWN1,W1];
IWN2=[IWN2,W2];
IC1=[IC1;C1];

IC2=[IC2;C2];

lkf=[lkf,k];
end
ksmax=max(lks)-1;
end
w1max=10^(8)*rho*Ceq1*lo*max(IWN1)/td11;
w2max=10^(8)*rho*Ceq1*lo*max(IWN2)/td11;

ttf=(tt*td11)*lkf;
ttr=(tt*td11)*lkm;
r=ones(size(lkm));
r=sqrt(tt*lkm);
e=(cputime-e);
%=============================          Plot data          ============================
%=================================================================================
plot(x,IC1'),title('Concentration tluene1 profiles'),grid, xlabel('normalized lenght'), ylabel('C1/Ceq1');pause

plot(x,IC2'),title('Concentration benzene2 profiles'),grid, xlabel('normalized lenght'),
ylabel('C2/Ceq1');pause

plot(ttf,10^(8)*rho*Ceq1*lo*IWN1/td11'),title('massfluxN1profile toluene g/cm3/s'),grid,xlabel(' time in
seconds'),ylabel('massfluxN1');pause


plot(ttf,10^(8)*rho*Ceq1*lo*IWN2/td11'),title('massfluxN2profiles benzene g/cm3/s'),grid,xlabel('time in
seconds'),ylabel('massfluxN2');pause

plot(r,IM),title('mass uptake versus sqrt(time)'),grid,xlabel('sqrt(normalized time)'),ylabel('M/Meq');pause

plot(ttr,IM),title('real mass uptake');grid,xlabel('time(hr)'), ylabel('IM'),pause
plot(log(ttr(2:L/numM)),log(IM(2:L/numM)));grid,title('log-log plot of real mass uptake');pause

plot(ttf,10^(8)*rho*Ceq1*lo*IWN2/td11','*',ttf,10^(8)*rho*Ceq1*lo*IWN1/td11),title('a la sortie : W1
toluene, W2 benzene (*) versus time in seconds'),pause

plot(x,IC1(20,:),x,IC2(20,:)*Ceq1/Ceq2,'*'),title('C1 toluene, C2 benzene (*) versus x'),pause,
%plot(x,C10,x,C20*Ceq1/Ceq2,'*'),title('C10 toluene, C20 benzene (*) versus x at 10s'),pause,

plot(C1,D11),title('D11 versus C1'),pause,
plot(C1,D12),title('D12'),pause,
plot(C1,D22),title('D22'),pause,
plot(C1,D21),title('D21 versus C1'),pause,
```

```
plot(C2,D11),title('D11 versus C2'),pause,
plot(C2,D12),title('D12'),pause,
plot(C2,D22),title('D22'),pause,
plot(C2,D21),title('D21 versus C2'),pause,
%plot(x,IC1(25,:),x,IC2(25,:)*Ceq1/Ceq2,'*'),title('C1toluene, C2benzene (*) versus x'),pause,

%=========================================================================

%save dtb000 IM IC1 IC2 IWN1 IWN2 ttf ttr r lkf ksmax N L r1 tt lo td11 td22 lo Cd1 Cd2 Ceq1 Ceq2
D10 D20 x rho w1max w2max fi0 rho1 rho2 rhop qsi12 qsi1p qsi2p D11 D22 D12 D21 M1 M2 ex;
```

```
%=========================================================================
%                                   sorption du benzène-chlorure de méthyl par epoxyde
%                                   (c1,c2,w) model  (article 5, chapter 8)
%=========================================================================

clc, clear,clf,format short,
e=cputime;
N=40;
num1=500;       num2=500;       numM=1;
L=10000;
r2=0.3;
r1=r2/N;
tt=r1/N;

%=========================  data for benzene2 - methylenechloride1 ==========================
zt=0; zb=0;
fi0=0.9;                    % toluene
lo=3.*10^(-3);              % (m)
%fi=ai*Ci;       rhoi*fi=Cdi=rho*Ci; rhoi== gammai;
xx=1;yy=1;qq=0;
rho1=0.88;                  %g/cm^3
rho2=0.87865;               %g/cm^3
rho=1.18;                   %g/cm^3
fip=1-0.0123-0.0117;
qsi12=0.0;
qsi2p=4.2;
qsi1p=4.2;
M1=84.2;
M2=78;

Cd1=5.1*10^(-3);            %g/cm^3
Cd2=0.5*10^(-3);            %g/cm^3
D10=1.93*10^(-10)*M1;               % m^2/s
D20=M2*1.44*10^(-10);               % m^2/s
Ceq1=Cd1/rho;
Ceq2=Cd2/rho;
Cdp=rho-Cd1-Cd2;
rhop=Cdp/fip;
a1=rho/rho1;
a2=rho/rho2;
ap=rho/rhop;
ex=exp(zt*Cd1+zb*Cd2);
td11=(lo^2/D10);            % s
td22=(lo^2/D20);            % s
b1=td11/td22;
VVV2=0.894*10^(-4);
VVV1=0.554*10^(-4);
p=VVV1/VVV2;
count=1;count1=1;
```

```
Cn=10^(-5);
C1=Cn*ones(1,N+1);     CC1=C1;                IC1=[ ];
C2=Cn*ones(1,N+1);     CC2=C2;                IC2=[ ];

CC1(1)=1; C1(1)=1;                    CC1(N+1)=CC1(N);C1(N+1)=C1(N);
CC2(1)=Ceq2/Ceq1; C2(1)=Ceq2/Ceq1;

%V1=Cn*ones(1,N+1);   V1(1)=1;               VV1=V1;              IV1=[ ];
V2=Cn*ones(1,N+1);     V2(1)=b1;             VV2=V2;              IV2=[ ];

%W1=Cn*ones(1,N+1);   W1(1)=1;               WW1=W1;              IW1=[ ];
W2=Cn*ones(1,N+1);     W2(1)=b1*(Ceq2/Ceq1); WW2=W2;              IW2=[ ];
IM=[ ];                Ikm=[ ]

D11=ones(1,N+1);       D12=zeros(1,N+1); D21=zeros(1,N+1);    D22=ones(1,N+1);
De22=1000;             % Case II
```

```
%=============================================================================

for i=1:N+1
x(i)=(i-1)/N;
end

%=========================          time loop          ========================

for k=1:L

W2(i)=WW2(1)-tt*b1*WW2(1)/De22;

%H=1-Ceq1*CC1-CC2*Ceq1;
H=ones(1,N+1);

for i=2:N

W2(i)=WW2(i)-r1*H(i)*(WW2(i)*VV2(i)-WW2(i-1)*VV2(i-1))-
(1/De22)*b1*(tt*WW2(i)+r1*b1*H(i)*D21(i)*(CC1(i)-CC1(i-1))+r1*b1*D22(i)*H(i)*(CC2(i)-CC2(i-1)));

C2(i)=CC2(i)-r1*H(i)*(WW2(i)-WW2(i-1));

C1(i)=CC1(i)+r2*H(i)*(D11(i+1)*CC1(i+1)-(D11(i+1)+D11(i))*CC1(i)+D11(i)*CC1(i-
1))+r2*H(i)*(D12(i+1)*CC2(i+1)-(D12(i+1)+D12(i))*CC2(i)+D12(i)*CC2(i-1));
end

W2(N+1)=0; C2(N+1)=C2(N);C1(N+1)=C1(N);

%=========================          Calcul des Dij          ========================

Cp=1-Ceq1*C1-xx*Ceq1*C2;      fi1=a1*Ceq1*C1;          fi2=xx*a2*Ceq1*C2;

D11=(1./(Cp)).*(a1*(1-Ceq1*C1).*(1-2*fi1*qsi1p)-xx*(M2/M1)*(D20/D10)*(qsi12-qsi1p-
qsi2p*p)*fi1.*fi2).*exp(tho*Ceq1*(zt*C1+zb*C2));
```

```
D12=(1./(Cp)).*((qsi12-qsi1p-qsi2p*p)*a2*fi1.*(1-Ceq1*C1)-(M2/M1)*(D20/D10)*p*(1-
2*qsi1p*fi2).*fi1).*exp(rho*Ceq1*(zt*C1+zb*C2));

D21=(1./(Cp)).*((a1*(1-Ceq1*C2).*fi2-(M1/M2)*(D10/D20)*fi1.*fi2)*(qsi12-qsi1p-
qsi2p*p)).*exp(rho*Ceq1*(zt*C1+zb*C2));

D22=(1./(Cp)).*(p*a2*(1-Ceq1*C2).*(1-2*qsi2p*fi2)-xx*(M1/M2)*(D10/D20)*fi1.*fi2.*(qsi12-qsi1p-
qsi2p*p)).*exp(rho*Ceq1*(zt*C1+zb*C2));

%=========================================================================

V2=W2./C2;

%=========================%=========================%=====================

CC1=C1;          CC2=C2;          C1(1:15),Ceq1*C2(1:18)/Ceq2,
VV2=V2;          WW2=W2;

%=================          massuptake          =================
if( rem(k,numM)==0)
Ikm=[Ikm,k];
C=Ceq1*(C1+xx*C2)/(Ceq1+xx*Ceq2);
RC=(1-Ceq1-xx*Ceq2)*C./(1-Ceq1*C);
M=0.0;
sum1=0.0;
for i=2:2:N
sum1=sum1+RC(i);
end
sum2=0.0;
for i=3:2:N-1
sum2=sum2+RC(i);
end
M=(1/(3*N))*(RC(1)+RC(N+1)+4*sum1+2*sum2);
IM=[IM,M];
end
%=================          Store data          =================
if(k<=1000 & rem(k,num1)==0)
count=count+1;
%IWN1=[IWN1,W1(N+1)];
IWN2=[IWN2,W2(N+1)];
IC1=[IC1;C1];
%IV1=[IV1;V1];
%IW1=[IW1;W1];
IC2=[IC2;C2];
IV2=[IV2;V2];
IW2=[IW2;W2];
Ikf=[Ikf,k];
Iks=[Iks,count];
end
if( k>1000 & rem(k,num2)==0)
count=count+1;
Iks=[Iks,count];
%IWN1=[IWN1,W1(N+1)];
```

```
IWN2=[IWN2,W2(N+1)];
IC1=[IC1;C1];
%IV1=[IV1;V1];
%IW1=[IW1;W1];
IC2=[IC2;C2];
IV2=[IV2;V2];
IW2=[IW2;W2];
Ikf=[Ikf,k];
end
ksmax=max(Iks)-1;
end
%w1max=10^(3)*rho*Ceq1*lo*max(IWN1)/td11;w2max=10^(3)*rho*Ceq1*lo*max(IWN2)/td11;
IC=Ceq1*(IC1+xx*IC2)/(Ceq1+xx*Ceq2);
ttf=(tt*td11/60)*Ikf;
ttr=(tt*td11/60)*Ikm;
r=ones(size(Ikm));
r=sqrt(tt*Ikm);
e=(cputime-e);
%========================        Plot data        ========================
%=============================================================================
plot(x,IC1'),title('Concentration1 profiles'),grid, xlabel('normalized lenght'), ylabel('C1/Ceq1');pause
plot(x,Ceq1*IC2/Ceq2'),title('Concentration2 profiles'),grid, xlabel('normalized lenght'), ylabel('C2/Ceq1');
pause
plot(x,IC'),title('Concentration totale profiles'),grid, xlabel('normalized lenght'), ylabel('IC'); pause
plot(r,IM),title('mass uptake versus sqrt(time)'),grid,xlabel('sqrt(normalized time)'),ylabel('M/Meq'); pause
plot(ttr,IM),title('real mass uptake');grid,xlabel('time(min)'), ylabel('IM'),pause
plot(log(ttr(2:L/numM)),log(IM(2:L/numM)));grid,title('log-log plot of real mass uptake');pause
plot(C1,D11),title('D11 versus C1'),pause,
plot(C1,D12),title('D12'),pause,
plot(C1,D22),title('D22'),pause,
plot(C1,D21),title('D21 versus C1'),pause,
plot(C2,D11),title('D11 versus C2'),pause,
plot(C2,D12),title('D12'),pause,
plot(C2,D22),title('D22'),pause,
plot(C2,D21),title('D21 versus C2'),pause,


%save ddtb009 IM IC1 IC2 IC ttf ttr r Ikf ksmax  N L r1 r2 tt  lo td11 td22 lo Cd1 Cd2 Ceq1 Ceq2 D10
D20 x rho fi0 rho1 rho2 rhop qsi12 qsi1p qsi2p D11 D22 D12 D21 b1 num1 num2 numM;
```